DIRECTOR OF INDUSTRIES
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GLYCERINE

ITS PRODUCTION, USES, AND EXAMINATION

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ITS PRODUCTION, USES AND EXAMINATION

FOR

CHEMISTS, PERFUMERS, SOAPMAKERS, PHARMACISTS
AND EXPLOSIVES TECHNOLOGISTS

BY

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TRANSLATED FROM THE GERMAN SECOND EDITION BY

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WITH SEVEN ILLUSTRATIONS

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PREFACE TO SECOND GERMAN EDITION.

GLYCERINE belongs to those substances which are made extensive use of in numerous branches of chemical technology. It is not only the raw material for the production of nitro-glycerine, but is also employed in very considerable quantities, increasing year by year, in many other industries. The soap-maker and perfumer, the chemist and druggist, the dyer, and many others use this substance for their purposes. That it therefore occupies a very important position needs no further explanation.

The necessity for a new edition of this book gives the author the welcome opportunity to include an account of all the new processes proposed for the production, purification, and extended use of glycerine. The book is therefore anew a compendium of all worth knowing on that subject, wherein is also fully described the employment and the production of derivatives of glycerine, especially the preparation of nitro-glycerine, the examination of nitro-glycerine-containing explosives, the use of glycerine in the manufacture of toilet soaps, in perfumery, etc. Each section has been re-written to correspond to the recent developments, and especially is described the examination of glycerine, and its determination in wine, beer, etc.

The author wishes and hopes that the second edition of his work will meet with the same approbation that the first enjoyed.

S. W. KOPPE.

1913.

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GLYCERINE.

INTRODUCTION

GLYCERINE belongs to those substances which have long been known; it was discovered by Scheele in 1779—but it has only found extensive application more recently, as it only then became possible to produce it on a large scale, it having previously been regarded as a by-product of but little importance.

The close study of glycerine produced in the pure state, shows that this body possesses properties which render it particularly suitable for the production of toilet preparations as well as for many medical purposes. The properties possessed by the substance obtained by the nitration of glycerine are technically of the greatest importance, since these serve for the production of the most powerful explosives yet known.

In addition to the last-named purpose, glycerine is actually used in large quantities in the manufacture of fine soaps and toilet preparations, and on account of its action on the skin it is a toilet article of the first rank.

By far the largest quantity is used for the production of nitro-glycerine, and thence the preparation of explosive products; it is also used, in the second place, in the manufacture of soaps and perfumery.

The discovery of glycerine took place, as has already been mentioned, in the year 1779, and the credit for its discovery belongs to the chemist Scheele, since he carried out a close investigation on the substance formed by the treatment of fats with litharge. Scheele already recognized one of the characteristic properties of this newly discovered body, viz. its intensely sweet taste, and called it on that account "sweet oil"; it was also occasionally spoken of as "fat-sugar".

The name *glycerine* derived from the Greek word γλυκυς = sweet, was first employed by Chevreul in the year 1811, and this chemist also studied in some detail the properties of glycerine in relation to its chemical constitution and decomposition products. Although now the industry has at its disposal considerable quantities of glycerine in the lyes from soap-making, it was formerly not produced on the manufacturing scale, since no suitable method for the recovery of pure glycerine on the large scale was known, nor any application for the substance itself.

In the year 1821, when the production of crystalline fatty acids on the large scale for the manufacture of stearine candles was commenced, it became urgently necessary to seek some application for the glycerine also separating in this manufacture in large quantities as a by-product. It required, however, still a relatively very long time before it was possible to produce glycerine itself in a highly pure state and at the same time in considerable quantity. The credit for having first introduced very pure glycerine into commerce probably belongs to the firm of Sarg in Liesing, near Vienna, who at the end of the year 1850 first produced glycerine clear as water and odourless; in England, Prices' Patent Candle Co., of London, appeared on the market with the new product about the same time as Sarg in Vienna.

Of the artificial compounds obtained from glycerine, nitro-glycerine is unquestionably that of most technical importance. This compound was discovered by Sobrero in the year 1847, but it did not attain other than scientific importance; it was through the work of the Swedish engineer Nobel, in 1863, that nitro-glycerine first came into technical notice as an explosive material of any importance, and this new explosive has first made possible the execution of the vast tunnels, and other works of modern times, in a very short time, e.g. Mont Cenis, St. Gothard, Arlberg, Simplon, etc.).

How extensive, moreover, is the applicability of glycerine is shown by the following summary of the purposes for which it is used. The most important of these applications we shall have to discuss in more detail later.

Glycerine is used: for extraction of hops, as an addition to wine (forbidden by law), in the manufacture of liqueurs, for the production of lemonade, punch essence, sweetmeats, in chocolate-making to prevent the drying of the chocolate, in fruit preserving, for the preservation of white of egg, yolk of egg, and flesh, in mustard-making, as an addition to vinegar, chewing and snuff tobacco, in cosmetics and numerous toilet articles, as cold cream, pomade, skin and hair remedies, in perfume manufacture for extraction of the more delicate floral scents, which are destroyed by distillation. It is used in finishing, in spinning and weaving, for production of not dry dressed muslin, in tanning, dyeing, and calico-printing, for production of parchment and coloured paper, in the manufacture of artificial wool, for softening and keeping moist driving belts, sole leather, modelling, etc., in glue and gelatine making, in the production of printing rollers and hectograph blocks, as also elastic blocks, for filling gas meters, hydraulic presses, and floating compasses, for lubricating clocks and machinery, for keeping guns clean, for production of copying inks, inks for stamping, and copying-paper, in the manufacture of paper-hangings and soaps, in the iron foundry for the manufacture of cast-iron, in photography, for the manufacture of blacking, luting, hot-water heating, etc. The largest quantity is, however, employed for the production of nitroglycerine and dynamite, while it also serves for the manufacture of formic acid, allyl alcohol, and artificial mustard oil.

Glycerine is used, moreover, for the preservation of anatomical specimens and the lymph for vaccination, for extraction of pepsin, for the preparation of liniments, salves, injections, for keeping moist pill and tablet masses, for court-plaster, and gelatine capsules, as solvent for medicinal substances, as remedy for chapped skin, for earache, for skin-diseases, etc.

CHAPTER I.

THE CHEMICAL PROPERTIES OF GLYCERINE.

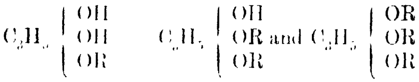
GLYCERINE, so far as at present known, does not occur in nature in the free state, but exists in very many combinations, and can be produced by established chemical processes. As was shown by Chevreul in the first quarter of the last century, true fats, whether of the animal or of the vegetable kingdom, exist as combinations of various acids with glycerine. Since, then, in all animal and vegetable organisms fat is found, we can describe glycerine as a universally disseminated product in animal and vegetable bodies.

We also know, moreover, various processes by which certain definite quantities of glycerine are produced, and the most interesting of those is the fermentation of spirituous liquors. If one allows wine-must or sweet-wort to ferment, there is formed, besides alcohol and carbon dioxide, a certain quantity of glycerine as a fermentation-product. By allowing one of the above-mentioned liquids, or even pure sugar solution, to ferment, one obtains besides alcohol, glycerine and succinic acid, and that in pretty considerable quantity; for example, from numerous researches, wine contains up to 2 per cent glycerine, while in beer 0·3 per cent may be found. By the many processes which take place during the production of rancidity in fats, glycerine is also formed, being liberated in the free state. If one exposes palm oil, a fat very liable to become rancid, for several months in thin layers to the air, and then extracts with water, the presence of glycerine is readily detected.

As regards chemical constitution, glycerine is an alcohol, a trihydric alcohol, that is one in which three atoms of hydrogen are replaceable by a monobasic acid radicle. By such substitution, compounds are obtained which are known as ethers or esters. Fats are then ethers, esters, or glycerides.

The composition of glycerine may be expressed by the formula $C_3H_8O_3$, having regard to the fact that in the three hydroxyl groups, which are present in glycerine, all the hydrogens may be replaced by an acid radicle, one has the rational formula for glycerine $C_3H_5(OH)_3$.

Expressing by R a monobasic acid radicle, the following compounds with glycerine are possible:—



$$C_3H_5\left|\begin{array}{l}OH\\OH\\OR\end{array}\right. \qquad C_3H_5\left|\begin{array}{l}OH\\OR\\OR\end{array}\right. \text{ and } C_3H_5\left|\begin{array}{l}OR\\OR\\OR\end{array}\right.$$

Compounds of the above constitutions may be produced artificially; the glycerine compounds or glycerides occurring in nature, are compounds in which all three substituted hydrogen atoms are replaced by an acid radicle. Stearic acid has the composition $C_{18}H_{36}O_2$, the glyceride of stearic acid occurring in fats is tristearin, of the formula $C_3H_5(OC_{18}H_{35}O)_3$.

Palmitic acid, $C_{16}H_{32}O_2$, and oleic acid, $C_{18}H_{34}O_2$, occur in fats likewise, as tripalmitin, and triolein respectively, and accordingly many fats are mixtures made up of various proportions of tristearin, tripalmitin, and triolein, or simply stearin, palmitin, and olein, while others consist of similar glycerides, as linolin in linseed oil, etc. The fats obtained from sheep, cattle, and hogs, as also cocoanut oil, palm oil, nutmeg butter, etc., belong to the first-named group, and have the following composition

$C_3H_5(OC_{18}H_{35}O)_3$	stearin
$C_3H_5(OC_{16}H_{31}O)_3$	palmitin
$C_3H_5(OC_{18}H_{33}O)_3$	olein

If one treats one of the above-mentioned compounds, or a mixture thereof, i.e. a naturally occurring fat, with a metallic hydroxide, the glyceride is decomposed in such a way that the glyceryl, C_3H_5, adds on three hydroxyl groups, 3OH, and glycerine is produced. This process, which is carried out on the large scale, is that which is generally expressed by the name saponification.

$$\underset{\text{tristearin}}{C_3H_5(OC_{18}H_{35}O)_3} + \underset{\substack{\text{potassium}\\\text{hydroxide}}}{3KHO} = \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\substack{\text{potassium}\\\text{stearate}}}{3KOC_{18}H_{35}O}$$

If one uses, instead of potassium hydroxide, the hydroxide of a metal like calcium, lead, etc., which forms with the fatty acids an insoluble compound, the glycerine is obtained in solution in the pure condition, and this was the method by which one was accustomed formerly to prepare glycerine.

In addition to this method, which is one of the treatments by which one produces glycerine in quantity, glycerine can also be produced by various other methods also in quantity, but we will return to these methods when dealing with the commercial production of glycerine.

One interesting preparation of glycerine, from the theoretical point of view, is that by which acetone is reduced with formation of glycerine.

Glycerine can be obtained from acetone by mixing the latter with zinc and acetic acid: the liberated hydrogen causes the reduction of the acetone into isopropyl alcohol according to the following equation:

$$\underset{\text{acetone}}{C_3H_6O} + \underset{\text{hydrogen}}{H_2} = \underset{\text{isopropyl alcohol}}{C_3H_7(OH)}$$

By treatment with zinc chloride water is removed from the isopropyl alcohol, and it becomes propylene.

$$\underset{\text{isopropyl alcohol}}{C_3H_7(OH)} - \underset{\text{water}}{H_2O} = \underset{\text{propylene}}{C_3H_6}$$

By treatment of propylene with iodine chloride, one obtains propylene iodochloride C_3H_6ClI, and from this, by the action of chlorine in presence of water, chlorpropylene, $C_3H_6Cl_2$, is produced. This compound is treated once more with iodine chloride in sealed tubes at a temperature of 140° C., when it is converted into trichlorhydrin, $C_3H_5Cl_3$. If this is heated with caustic potash, glycerine and potassium chloride are produced:

$$\underset{\text{trichlorhydrin}}{C_3H_5Cl_3} + \underset{\substack{\text{potassium}\\\text{hydroxide}}}{3KOH} = \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\substack{\text{potassium}\\\text{chloride}}}{3KCl}$$

CHAPTER II.

COMPOUNDS AND DECOMPOSITION PRODUCTS OF GLYCERINE.

THE relationship of glycerine with the substances known as "alcohols" is proved by the fact that glycerine forms compounds which are similar in composition to those of other alcohols. Ordinary alcohol (ethyl alcohol) can be changed into ethyl ether by abstraction of water; under similar conditions glycerine gives glycerine ether (ester); ethyl alcohol forms with acids certain definite compounds; glycerine behaves in quite a similar way.

The compounds of glycerine are of practical interest, in so far as possibly the one or the other may appear as an intermediate product in the production of glycerine on the large scale, e.g. the compound which glycerine forms with sulphuric acid

GLYCERO-SULPHURIC ACID.

In the production of this compound, one mixes two parts by measure of concentrated sulphuric acid with one part of concentrated glycerine, with continuous stirring, whereby the mixture becomes intensely hot; afterwards the mixture is cooled to the ordinary temperature, diluted strongly with water, and milk of lime added until the liquid has no longer an acid reaction. At the bottom of the vessel is thrown down a precipitate of gypsum, whilst the supernatant liquid is a solution of calcium glycero-sulphate; by concentrating by evaporation, and cooling this solution, one obtains the salt in the form of crystals.

In order to obtain the glycero-sulphuric acid in the free state, one adds the cold prepared solution of the calcium glycero-sulphate to exactly so much oxalic acid solution as is necessary for the neutralization of the lime; there separates heavy insoluble calcium oxalate in the form of a granular precipitate, whilst the glycero-sulphuric acid remains in solution.

The compound is so unstable, that it is decomposed by merely warming the solution; in order, therefore, to obtain it in the anhydrous condition, one must free it from water under the receiver of an air-pump, and over sulphuric acid, and thus obtain finally the pure glycero-sulphuric acid in the form of a colourless, sour tasting syrup, which compound, having regard to the dibasic character of sulphuric acid, must be written as $C_3H_5(OH)_2(OSO_2OH)$. The formation of glycero-sulphuric acid may be represented by the following equation:—

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\substack{\text{sulphuric}\\ \text{acid}}}{H_2SO_4} = \underset{\substack{\text{glycerine-sulphuric}\\ \text{acid}}}{C_3H_5(OH)_2(OSO_3H)} + \underset{\text{water}}{H_2O}$$

Glycero-sulphuric acid is formed as an intermediate product in the decomposition of fats by means of acid in the so-called "acid saponification"; whilst from the glyceride, e.g. tristearin, stearic acid is formed, the glycerine in the moment of its liberation unites with the sulphuric acid. But in the decomposition of fats by acid, higher temperatures are employed, so that the glycero-sulphuric acid is immediately again decomposed into glycerine and sulphuric acid, and this latter is once more available for the decomposition of fresh fat.

Glycerine Ether.

As is well known, ordinary alcohol forms, when warmed with sulphuric acid, a compound, ethyl sulphuric acid, which is a compound completely analogous to glycerine sulphuric acid; by heating above 140° the ethyl-sulphuric acid decomposes into ethyl ether and sulphuric acid.

By treating very concentrated (anhydrous) glycerine at a high temperature, with concentrated sulphuric acid, not only is the first-formed glycerine-sulphuric acid decomposed into its constituents, but water is also removed from the glycerine, and acrolein is produced, owing to the great dehydrating action of sulphuric acid, which is not exhausted even by the hydroxyl groups of glycerine:

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} = \underset{\text{acrolein}}{C_3H_4O} + \underset{\text{water}}{2H_2O}$$

We shall have to return later to the properties of acrolein itself, since it is one of the frequently appearing decomposition products of glycerine, and is of practical importance in the study of fats.

By treating glycerine with substances which act less energetically than sulphuric acid at high temperatures, only little acrolein is formed, but chiefly glycerine ether. For the production of glycerine ether, one heats in a spacious distillation apparatus 1 parts of concentrated glycerine with 3 parts of powdered calcium chloride. The mass froths on warming strongly, and gives off between 170° and 175° copious vapours of glycerine ether $(C_3H_5)_2O_3$. This can be again reduced to glycerine by prolonged heating with water.

GLYCERO-PHOSPHORIC ACID.

By treating concentrated glycerine with glacial phosphoric acid glycero-phosphoric acid is produced; one neutralizes the liquid with barium carbonate, decomposes the solution of barium glycero-phosphate with sulphuric acid, and concentrates the solution in vacuo to a syrupy consistency. By heating, the compound is decomposed.

Glycero-phosphoric acid, hitherto of no practical importance, is a very interesting body to the physiological chemist, because it forms an essential constituent of the nerve substance of the alveolus, and of egg-yolk.

By treating glycerine with haloid acids, or with phosphorus iodide, nitric acid, etc., one can produce from glycerine a great number of substituted compounds; up till now only one of these substitution products, viz. the nitro-product, finds employment technically. We can therefore limit ourselves to a merely brief description of these bodies having only theoretical importance.

THE CHLORHYDRINS.

By treating glycerine with hydrochloric acid, a number of compounds are formed, which are interesting examples of the substitution process, and throw considerable light on the constitution of glycerine.

Hydrochloric acid acts on glycerine in various ways according to the temperature and pressure. When a current of hydrochloric acid gas is passed through glycerine so long as it is absorbed by the liquid, in a closed tube and heated up to the boiling-point of water, the product neutralized with potassium carbonate, and extracted with ether, a liquid is obtained, whose boiling-point is 220° C., specific gravity 1·4, and which has a sweet taste. This liquid is the simple chlorhydrin, or monochlorhydrin, having the constitution $C_3H_5(OH_2)Cl$. The reaction may be represented by the following equation:—

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\substack{\text{hydrochloric}\\\text{acid}}}{HCl} = \underset{\text{water}}{H_2O} + \underset{\text{monochlorhydrin}}{C_3H_5(OH_2)Cl}$$

By heating glycerine with about fifteen times its weight of hydrochloric acid in a closed tube up to 100° C. for ten to twelve hours, one obtains by subsequent distillation an ethereal fragrant liquid, having specific gravity 1·383, and boiling-point 174° C. This is dichlorhydrin, $C_3H_5(OH)Cl_2$.

$C_3H_5(OH)_3$	$+$	$2HCl$	$=$	$2H_2O$	$+$	$C_3H_5(OH)Cl_2$
glycerine		hydrochloric acid		water		dichlorhydrin

Since there are three hydroxyl groups in glycerine which can be replaced by other radicles, it must form a trichlorhydrin. This, however, is not produced by the direct action of hydrochloric acid on glycerine, but can only be obtained in an indirect way. By treating dichlorhydrin with phosphorus pentachloride, trichlorhydrin is produced in the following manner.

$C_3H_5(OH)Cl_2$	$+$	PCl_5	$=$	HCl	$+$	$POCl_3$	$+$	$C_3H_5Cl_3$
dichlorhydrin		phosphorus penta chloride		hydro chloric acid		phosphorus oxychloride		trichlor-hydrin

Trichlorhydrin has a specific gravity of 1·417, boils at 155 C., and may be regarded as glycerine in which all three hydroxyl groups are replaced by chlorine. By long continued heating of trichlorhydrin with water at a high temperature in a sealed tube, it is again broken up into hydrochloric acid and glycerine, a proof that the radicle C_3H_5 (glyceryl) has remained intact.

When trichlorhydrin is treated with chlorine gas, one of the hydrogen atoms of the C_3H_5 radicle is replaced by chlorine, with the production of tetrachlorhydrin, $C_3H_4Cl_4$.

The constitution of the molecule is easily understood, if one assumes that the atoms in the glycerine molecule are arranged in a similar way to that in marsh gas; we then have two hydroxyl groups attached directly to the carbon atom, and more easily substituted by chlorine than that which takes the place of hydrogen in one of the methyl groups. The following formulæ will make this relationship clear:—

$$\text{Marsh gas C}\left\{\begin{array}{l}\mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\\ \mathrm{H}\end{array}\right. \qquad \text{Glycerine} = \mathrm{C}\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{array}\right.$$

$$\text{Monochlorhydrin C}\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2OH}\\ \mathrm{OH}\\ \mathrm{Cl}\end{array}\right. \qquad \text{Dichlorhydrin C}\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2OH}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{array}\right.$$

$$\text{Trichlorhydrin C}\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CH_2Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{array}\right. \qquad \text{Tetrachlorhydrin C}\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{CHCl\ \ Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{array}\right.$$

There is also another compound which may be regarded as an intermediate product in the above substitutions, viz. epichlorhydrin. It is obtained when dichlorhydrin is treated with aqueous potash solution. This is a liquid boiling at 118° C., which by treatment with hydrochloric acid is again changed into dichlorhydrin.

$$\underset{\text{dichlorhydrin}}{\mathrm{C_3H_5(OH)Cl_2}} + \underset{\substack{\text{potassium}\\ \text{hydroxide}}}{\mathrm{KOH}} = \underset{\substack{\text{potassium}\\ \text{chloride}}}{\mathrm{KCl}} + \underset{\text{epichlorhydrin}}{\mathrm{C_3H_5OCl}}$$

$$\underset{\text{Epichlorhydrin}}{\mathrm{C_3H_5OCl}} + \mathrm{HCl} = \underset{\text{Dichlorhydrin}}{\mathrm{C_3H_5(OH)Cl_2}}$$

By treatment of glycerine with hydrobromic acid, or phosphorus bromide, bromine derivatives are obtained which are similar in constitution to the chlorine-derivatives. These are as follows:—

Monobromhydrin — $C_3H_5(OH)_2Br$
Dibromhydrin $C_3H_5(OH)Br_2$
Tribromhydrin $C_3H_5Br_3$
Epibromhydrin C_3H_5OBr

By treating glycerine for twenty-four hours with an equal weight of phosphorus bromide, and then distilling up to incipient charring, one obtains besides acrolein, a distillate separating into two layers, the upper one being epibromhydrin, C_3H_5OBr, the lower one dibromhydrin, $C_3H_5(OH)Br_2$; the residue remaining in the retort, gives after neutralization and treatment with ether, besides dibromhydrin, also monobromhydrin, $C_3H_5(OH)_2Br$ When allyl bromide is mixed with bromine, tribromhydrin is produced :—

$$\underset{\text{allyl bromide}}{C_3H_5Br} + Br_2 = \underset{\text{tribromhydrin}}{C_3H_5Br_3}.$$

ACTION OF IODINE COMPOUNDS ON GLYCERINE.

If glycerine is treated with hydriodic acid, more energetic action takes place than with hydrochloric acid or hydrobromic acid; it immediately separates all the hydroxyl groups from the glycerine, with the formation of allyl iodide. The excess of hydriodic acid reacts further on the allyl iodide, and forms propylene:

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{hydriodic acid}}{3\,HI} = \underset{\text{allyl iodide}}{C_3H_5I} + 3H_2O + I_2$$

$$\underset{\text{allyl iodide}}{C_3H_5I} + HI = \underset{\text{propylene}}{C_3H_6} + I_2$$

Allyl iodide is prepared in the following way: In a tubulated retort are warmed a solution of

8 parts iodine in carbon bisulphide and 1 part of phosphorus, and after distilling off the carbon bisulphide, anhydrous glycerine is added in small quantities to the phosphorus iodide remaining. The two bodies react on each other with great violence, and from the resulting mass one obtains, by distillation, propylene, water, and allyl iodide.

The crude allyl iodide is brown coloured; it may be decolorized by shaking with caustic soda solution, rectified over calcium chloride, and is then obtained as a colourless liquid, boiling at 102° C., which has the sp. gr. 1.789, and a strong garlic-like odour. The propylene passing over as a by-product, by strong cooling and pressure, condenses to a colourless, peculiar-smelling liquid.

Glycerine is, as already stated, an alcohol, but it is a trihydric alcohol, whilst from the combination, C_3H_5, that is the radicle propenyl, one obtains a monohydric alcohol, allyl alcohol. This is then a proof that the radicle C_3H_5, which is contained in glycerine, is not quite identical with the radicle allyl. It may be quite readily distinguished by its different atomicity from the latter, to which, however, in many points it stands very near.

It is, moreover, possible to directly produce allyl alcohol from glycerine in the following manner. When one heats glycerine with oxalic acid up to 110° C., formic acid and carbon dioxide are produced; out of the diluted liquid, formic acid may be obtained by distillation. As regards combination of the formic acid with the glycerine, this is only induced at a higher temperature, and according to Tollens and Henninger, the operation is best carried out in the following manner. One mixes 4 parts glycerine with 1 part oxalic acid, and adds to the mixture ¼ to ½ part of ammonium chloride, when on heating one obtains a glyceride of formic acid (monoformin). By prolonged heating at 260° C. the monoformin is split up into allyl alcohol, carbon dioxide, and water:—

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{formic acid}}{CH_2O_2} = \underset{\text{glycero-formic acid}}{C_3H_5(OH)_2O.HCO} + \underset{\text{water}}{H_2O}$$

$$\underset{\text{glycero-formic acid}}{C_3H_5(OH)_2O.HCO} = \underset{\text{allyl alcohol}}{C_3H_5(OH)} + \underset{\text{carbonic acid}}{CO_2} + \underset{\text{water}}{H_2O}$$

Allyl alcohol begins to distil already at 195° C.; the distillation continues to 260° C., and simultaneously there also passes over acrolein from the direct decomposition of the glycerine itself. In order to obtain the allyl alcohol in a pure state, one shakes the raw distillate with a solution of potassium carbonate, whereby water and allyl formate are removed; the liquid separated from the potassium carbonate solution is washed with solid alkali, whereby the acrolein is removed. After rectification at 96° to 100° C., drying with caustic baryta, and repeated distillation, one obtains finally pure allyl alcohol as a colourless liquid, with a biting disagreeable smell, low specific gravity (0·858), and a boiling-point of 96° C.

ACROLEIN

Among the decomposition products of glycerine with which one has most frequently to do, acrolein takes the first place, because glycerine by rapid heating very easily becomes converted into this body, and even in combined glycerine (in fats) the same decomposition takes place, if one heats the fat quickly, the disagreeable smell which is evolved when one drops fat on a hot plate or allows it to fall on glowing coal, is caused by the evolution of acrolein itself.

By rapid distillation of glycerine acrolein is also formed, and that in very large quantity at the end of the operation. It imparts to odourless glycerine, when it is present in even only minute quantity, a disagreeable and penetrating smell.

For the production of acrolein in a large quantity one treats anhydrous glycerine with strong dehydrating substances, and at high temperatures e.g. one heats 1 part glycerine with 2 parts of acid potassium sulphate, whereby the decomposition of the glycerine takes place according to the following equation

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} \qquad \underset{\text{acrolein}}{C_3H_4O} + \underset{\text{water}}{2H_2O}$$

One obtains acrolein by rectification as a colourless liquid which boils at 52° C., the vapours of which attack the eyes and nose with very great violence, and cause great inflammation; in water it dissolves only slightly, but in alcohol on the other hand very easily. Acrolein has the power to reduce silver oxide, and is thereby changed into acrylic acid, of which the formula is $C_3H_4O_2$.

A very interesting decomposition of glycerine is that which takes place by the action of ferments on dilute glycerine, and by which acids of the fatty acid series are formed.

One adds glycerine to a liquid which is undergoing alcoholic fermentation, when soon after the addition of a certain quantity of glycerine the fermentation ceases, so that glycerine must be regarded as a body inimicable to alcoholic fermentation. Those ferments of the lower order, which are known as bacteria, are able, however, to decompose glycerine, and thereby give rise to a whole series of acids belonging to the fatty acid series.

One allows to stand a mixture of 1 part glycerine, 12 parts water, ½ part chalk, and 0.12 part freshly comminuted mutton at a temperature of 35-40° C., so takes place a very slow fermentation process, which consists of a whole series of distinct fermentations, some taking place side by side, others in sequence; carbon dioxide and hydrogen gas are evolved.

The whole fermentation lasts about eight months, during which are formed, besides ethyl alcohol, acetic, propionic, butyric, valerianic, and caproic acids, as well as a small quantity of higher fatty acids—the greater part of the glycerine is hereby decomposed.

The fermentation processes, which in this case are known to take place, are the alcoholic fermentation, the acetic acid fermentation, and the butyric acid fermentation. With yeast glycerine ferments at 20 to 30°, with the formation of propionic acid; with the butyric acid bacillus, up to butyl alcohol and trimethyleneglycol.

GLYCERIDES

The action of acids on glycerine has been fairly completely studied and has been already referred to on p. 7. By bringing together glycerine and acids, compounds are formed which are described as ethereal compounds. The most important technically of these compounds are the fats. As the constitution of the fats became better known, it was important to determine whether by direct combination of acids contained in fats with glycerine, compounds could be obtained similar in their properties to the fats.

The reaction attains completion when glycerine is mixed together with stearic acid, palmitic acid, or oleic acid, there is formed according to the proportions in which the acids are employed, the mono-, di-, and triglycerides of the respective fatty acids. The naturally occurring fats are triglycerides, and the compounds produced artificially resemble completely the naturally occurring fats both as regards their physical and their chemical properties.

By the combination of glycerine with the acids, water is always eliminated, and in the synthesis of the glyceride tristearin, for example, the following reaction takes place:

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{stearic acid}}{3(C_{18}H_{36}O_2)} = \underset{\text{stearic glyceride}}{C_3H_5(OH_{18}C_{35}O)_3} + \underset{\text{water}}{3\,H_2O}$$

Besides the glycerides of oleic, palmitic, and stearic acids, which commonly occur in fats, one has also the various glycerides of the other acids of the fatty acid series (formic, butyric, propionic, valerianic, etc.); as far as these acids occur in nature in the form of glycerides, the artificially produced compounds resemble in all respects the natural. Triacetin, tributyrin, trilaurin, are such glycerides which are met with in nature. One can prepare the glycerides by various methods either by heating glycerine with the respective acid in sealed glass tubes in an oil bath, or by mixing sulphuric acid as well as the fatty acid with the glycerine or by dissolving the acid in the glycerine by warming, and then passing hydrochloric acid gas through the solution.

The action of sulphuric acid in the synthesis of the glycerides of the other acids may be explained by the formation in the first place of glycero-sulphuric acid, which, however, in contact with the organic acids is converted into the glyceride of the acid, and into free sulphuric acid. For example:—

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{sulphuric acid}}{H_2SO_4} = \underset{\text{glycerine sulphuric acid}}{C_3H_5(OH)_2(O.SO_3H)} + \underset{\text{water}}{H_2O}$$

$$\underset{\text{glycero-sulphuric acid}}{C_3H_5(OH)_2(O.SO_3H)} + \underset{\text{palmitic acid}}{3(C_{16}H_{32}O_2)} = \underset{\text{tripalmitin}}{C_3H_5(OC_{16}H_{31}O)_3} + \underset{\text{water}}{2H_2O} + \underset{\text{sulphuric acid}}{H_2SO_4}$$

The action of hydrochloric acid is that chlorhydrin is first formed from the glycerine, which in contact with the acid is converted into the respective glyceride, water, and hydrochloric acid gas.

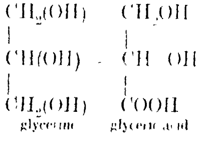
$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{hydrochloric acid}}{HCl} = \underset{\text{chlorhydrin}}{C_3H_5(OH)_2Cl} + \underset{\text{water}}{H_2O}$$

$$\underset{\text{chlorhydrin}}{C_3H_5(OH)_2Cl} + \underset{\text{oleic acid}}{3(C_{18}H_{34}O_2)} = \underset{\text{triolein}}{C_3H_5(O.C_{18}H_{33}O)_3} + \underset{\text{water}}{2H_2O} + \underset{\text{hydrochloric acid}}{HCl}$$

Nitric acid exerts a somewhat different reaction from other acids on glycerine, and indeed the reaction depends in a great degree on whether one employs dilute nitric acid, or that of high concentration. Nitric acid of low strength forms from glycerine a new acid, which is known as glyceric acid.

One can produce glyceric acid by introducing into a vessel nitric acid of specific gravity 1·5, and cautiously allowing to flow down the sides of the vessel a mixture of equal volumes of water and glycerine in such a way that the glycerine floats above the nitric acid; after about a week the liquid is placed in a desiccator over sulphuric acid, and is left there until a syrupy liquid is produced. This is neutralized with lead hydroxide, and the lead salt decomposed by hydrogen sulphide, whereby after again concentrating over sulphuric acid, glyceric acid is obtained as a faintly yellow liquid, easily soluble in water and alcohol.

The formula of glyceric acid is $C_3H_6O_4$, and one can represent its formation from glycerine in the following way:—



$$\underset{\text{glycerine}}{\begin{array}{l} CH_2(OH) \\ | \\ CH(OH) \\ | \\ CH_2(OH) \end{array}} = \underset{\text{glyceric acid}}{\begin{array}{l} CH_2OH \\ | \\ CH\ \ OH \\ | \\ COOH \end{array}}$$

or $C_2H_3(OH)_2COOH$. One can also regard it as dihydroxypropionic acid.

According to this equation only one of the two outside groups – CH_2OH, which are present in glycerine, is changed by the substitution of an oxygen atom for the two hydrogen atoms with the formation of the carboxyl – $COOH$; theoretically there is yet another glyceric acid, in which both the – $CH_2(OH)$ groups are changed in the same way. The production of this acid has not yet, however, been accomplished.

The powerful oxidizing action which nitric acid possesses, necessitates that the change in the glycerine does not take place so simply as the above-mentioned equation indicates; there are many more complex secondary reactions, and a part of the glycerine is consequently converted into racemic acid, glycollic acid, formic acid, and oxalic acid.

Very concentrated nitric acid acts on glycerine in such a way that a glyceride results, viz. the nitric acid triglyceride, or trinitroglycerine, of the formula $C_3H_5(O.NO_2)_3$.

The production of this substance will be described in more detail later.

As regards the production of the mono- and dinitroglycerides, one has to proceed in another way than that of direct combination of glycerine with nitric acid. They are obtained by making use of the monochlorhydrin or dichlorhydrin with a mixture of equal parts fuming nitric acid and sulphuric acid. By diluting the liquid with much water an oily liquid separates, which possesses the composition $C_3H_5Cl(O.NO_2)_2$ — dinitromonochlorglycerine or $C_3H_5Cl_2(O.NO_2)$ — mononitrodichlorglycerine.

Among the numerous compounds produced from glycerine by substitution processes, up till now only one has attained technical importance, and this is the nitroglyceride ester (erroneously known as nitroglycerine) which is distinguished by the property that it is decomposed by a blow with a violence which exceeds by far that of other explosive substances. In consequence of the property, the compound referred to is employed in technical explosives in ever increasing ways, and its manufacture forms a special industry.

CHAPTER III

THE PRODUCTION OF GLYCERINE

Up to the time that one required to separate stearic and palmitic acids from fats in a pure state for the purposes of candle manufacture, glycerine was only produced on the small scale for scientific research and pharmaceutical purposes, notwithstanding that in the spent lyes from soap manufacture one had the raw material in large quantity ready for employment. The ordinary practice of the pharmacist for the production of glycerine was to saponify oil with lead oxide, separate the liberated glycerine from the lead soap by washing with water, and then produce glycerine in the pure state from the still very impure solution by the method described below

Glycerine from Lead Soap.

One prepares lead soap (the emplastrum simplex, or diachylon plaster of the pharmacist) by stirring together 9 parts by weight of olive oil, 15 parts by weight of litharge, and a sufficiency of water until a uniform mixture is obtained, which is then boiled in an iron vessel with constant stirring and addition of boiling water, until on testing by cooling, it congeals to a viscous white mass, which has no longer any greasy feel.

Olive oil consists for the most part of the glyceride of oleic acid, while the glyceride of palmitic acid and a small amount of tristearin are also present; lead soaps are formed corresponding to each, the lead oleate predominating. The resulting mass is insoluble in water, softens on warming, but is hard when cold

For the separation of the glycerine mixed with the lead soap, one pours hot water on the completely boiled, but still fluid plaster, stirs the mass thoroughly, and leaves it at rest for a time in order that the soap may separate from the water, then pours this off, and repeats the washing several times, until all glycerine is separated from the mass; the glycerine waters are mixed, and the purification proceeded with.

As the excess of lead oxide dissolves in the glycerine, this must be first removed, which is accomplished *by passing sulphuretted hydrogen through* the glycerine. The lead is converted into sulphide, which is thrown down in the form of a black precipitate, and is removed from the glycerine by filtration. The liquid after freeing from lead is evaporated, and yields glycerine of a brown colour and unpleasant odour; to render it water-white, one allows the liquor to filter slowly through freshly burnt animal charcoal until it emerges perfectly colourless and odourless, and evaporates it finally on a water-bath to a syrupy consistency. This evaporation must be done, however, with great caution, as by contact with air, glycerine, especially if it has already reached a high concentration, again becomes dark coloured.

The glycerine obtained by this treatment is quite pure, and one obtains also a good yield of glycerine in relation to the quantity of oil used; at the present time, however, scarcely any glycerine is prepared in this way, as the cost of production is so heavy that the glycerine so produced is much dearer than the equally pure and highly concentrated product which is yielded by the stearic acid manufactory. Moreover, lead plaster is now increasingly rarely prepared from olive oil, being mostly made by directly saponifying with litharge oleic acid, which can be cheaply obtained as a by-product in stearic acid manufacture.

Production of Glycerine in the Stearic Acid Factory.

In works in which the so-called *stearic acid*, i.e. a mixture of stearic and palmitic acids, is produced, a very considerable quantity of glycerine results as a by-product, and it is worked up as a very valuable substance in all the larger works of this class, that is to say, concentrated and refined. The way in which this is carried out depends upon the process which has been employed for the decomposition of the fats, as will also the yield of glycerine obtained.

The decomposition of fats can be effected in many ways, either by saponification with alkalies or alkaline earths, as for example with quicklime, more rarely with caustic alkali, as in the older processes for stearine production, or by saponification with sufficient lime, which is a far less common method, to form calcium soap, with the simultaneous employment of high pressure steam.

Other methods for the separation of fatty acids from glycerine incorrectly termed saponification processes are those in which the decomposition of the fat is effected by means of acid, more especially by sulphuric acid; finally there is the use of even water itself in place of acids, the "saponification" being brought about with either superheated water or superheated steam.

These methods are all certainly adapted for the production of fatty acids for employment in the manufacture of stearine candles; they are not, however, equally suitable when, as at present in all works of this kind, it is a question of the production not only of fatty acids, but also of glycerine. Thus, for example, in the process of saponification with much acid and at high temperatures, the glycerine is entirely destroyed. It is for this reason that the process of saponification has to be modified, in order to ensure that so valuable a substance as glycerine is not lost.

The present work has for its object the description of glycerine and its applications. It lies, therefore, outside its scope to occupy ourselves very closely with the reactions which take place in the various processes mentioned above. We must confine ourselves then to merely outlining these processes in all brevity, and indeed only in so far as they have reference to the production of glycerine itself.

The reactions involved in the various methods for carrying out this process are theoretically as follows:

(*a*) In the saponification with alkalies, e.g. with lime:—

$$\underset{\text{stearin}}{2C_3H_5(OC_{18}H_{35}O)_3} + \underset{\text{calcium hydroxide}}{3Ca(OH)_2} = \underset{\text{calcium stearate}}{3Ca(C_{18}H_{35}O_2)_2} + \underset{\text{glycerine}}{2C_3H_5(OH)_3}$$

Since in fats in addition to stearin, palmitin and olein are also present, these glycerides are also decomposed in the same way as stearin, as given above; one obtains therefore a mixture of the lime salts of stearic acid, palmitic acid, and oleic acid (lime soaps insoluble in water) and a solution of glycerine.

(*b*) In the saponification with acids, e.g. with sulphuric acid:

$$C_3H_5(OC_{16}H_{31}O)_3 + 4H_2SO_4 = 3C_{16}H_{31}O(O.SO_3H) + \underset{\text{glycero-sulphuric acid}}{C_3H_5(OH)_2(OSO_3H)} + H_2O$$

and arising out of these compounds by addition of $4H_2O$:

$$\underset{\text{palmitic acid}}{3C_{16}H_{31}O(OH)} + \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{sulphuric acid}}{4H_2SO_4}$$

or, expressed in words, by the action of sulphuric acid on a glyceride, for example, palmitin, it is first of all decomposed in such a way that palmito-sulphuric acid, and glycero-sulphuric acid result with the separation of one molecule of water; both the first-mentioned compounds are split up by the action of water into palmitic acid, glycerine, and sulphuric acid, which last remains in solution along with the glycerine.

(*c*) By saponification with water at high temperatures, or with superheated steam:—

$$\underset{\text{stearin}}{C_3H_5(OC_{18}H_{35}O)_3} + \underset{\text{water}}{3H_2O} = \underset{\text{stearic acid}}{3C_{18}H_{35}O(OH)} + \underset{\text{glycerine}}{C_3H_5(OH)_3}.$$

1. SAPONIFICATION OF FATS BY MEANS OF CAUSTIC ALKALIES OR QUICKLIME

The oldest among the methods employed on the large scale for the production of fatty acids is that in which by making use of caustic alkalies, sodium or potassium compounds are produced identical with the ordinary boiled soaps. One obtains a potash or soda soap, out of which by treatment with a strong acid sulphuric or hydrochloric—the fatty acids separate, while the glycerine in the soap being liberated, passes into the liquor underneath.

As the complete saponification with caustic alkalies is somewhat costly, and the whole process moreover was accompanied by many practical difficulties, it had entirely gone out of practice, but was again brought into use by Mege-Mouries, with the alteration that the fat to be saponified is first divided by stirring with water at 45° C., with addition of a small percentage of soap, into exceedingly fine drops, and converted into the so-called "spherical state" (emulsified), and then can be very easily and quickly saponified, so that it gives a very largely increased yield of fatty acids, which reaches the maximum generally obtainable.

Among all the processes by which satisfactory saponification takes place, that formerly possessing the greatest importance is that in which quicklime was employed, as on the one hand quicklime is cheaply obtained, and on the other hand it also has the advantage that the lime soap is insoluble, and can therefore be easily separated from the liquid. It was carried out in the following manner:—

The process was commenced by mixing the fat—tallow, or palm oil—with water in large wooden or stone vessels, and the fat melted by passing in steam and heated to 100° C. With constant boiling one adds 15 per cent of the weight of fat employed of lime to the vessel. The lime employed must be iron-free, freshly burnt (free from carbonic acid) and broken down with water to a uniform lump-free milk, before addition to the fat.

One assists the saponification by the continuous passage of steam, and by the uninterrupted motion of the stirring gear. The commencement of the saponification shows itself by the thickening of the mass, an appearance which usually manifests itself three or four hours after the beginning of the operation. Later small particles of lime soap unite into small lumps, which rise to the surface. After the expiration of seven or eight hours the saponification is complete, and the vessel contains by this time a solid mass which, if the operation has been rightly carried out, consists only of lime soap together with any excess of lime used, and must be entirely free from little drops of undecomposed fat. The yellow or brown-coloured liquid to be found mixed with the lime soap (always depending on the quality of the fats employed), is a dilute solution of crude glycerine in water, which is contaminated by a large quantity of foreign matter

A modification of this process is that in which a much smaller quantity of lime suffices for saponification, if one allows the lime to act on the fat under a steam-pressure of about ten atmospheres Under these conditions it is sufficient to employ two to three per cent lime to bring about complete saponification, as acid lime salts are formed from the fatty acids.

As regards the production of glycerine, this process offers the advantage that one works with a far smaller quantity of water than in the process above described, and accordingly a more concentrated solution of glycerine results.

In both cases the lime soap produced is decomposed by sulphuric or hydrochloric acid, whereby is formed gypsum or calcium chloride, and the mixture of the three fatty acids, stearic, palmitic, and oleic, is freed as far as possible from oleic acid by pressure in very strong hydraulic presses, and employed, after refining, for the manufacture of stearine candles, whilst the liquid separated from the lime soap is utilized for the extraction of glycerine. To the quality of the raw and strongly diluted glycerine, which is different according to the method employed for the extraction, reference will be made later.

THE KREBITZ PROCESS.

The process for the decomposition of fats by lime, according as we have described it, possesses to-day only historic importance. It has still, however, a certain interest, as therefrom one of the newest treatments for the splitting of fats has been developed. Krebitz (D.R.P. 605, 108) has proposed the production of lime soap in the first instance, and this is then introduced into a boiling solution of carbonate of soda or potash which decomposes it into the alkali soap and carbonate of lime, Bottaro (D.R.P. 211, 969) again separates the free fatty acids from the lime soap by treatment with gaseous sulphurous acid. The correct preparation of the lime soap is essential, it is carried out by Krebitz in the following manner:—

The neutral fat, heated up to about 100 C., is intimately mixed with an equivalent mass of milk of lime prepared from pure lime, whereby a thick emulsion is first of all produced, which is left to stand quietly overnight protected from cooling. Thereby is formed finally a solid, though easily powdered lime soap, which is ground up and washed with water, in which it is insoluble, in order to remove the glycerine. The sufficiently washed soap powder is then, as already mentioned, treated with a solution of alkaline carbonate, whereby the decomposition into alkali soap and insoluble calcium carbonate is effected.

2. Decomposition of Fats by Sulphuric Acid

As has already been shown with formulæ, by the action of sulphuric acid on glycerides, compounds are produced of the fatty acids and the glycerine with sulphuric acid, and these are then decomposed by water into fatty acids, glycerine, and sulphuric acid. Although in all cases in which sulphuric acid is employed, these reactions must take place, the process is capable of being carried out in very different ways, and one distinguishes especially the saponification in the slow way, and the so-called rapid saponification or fractional saponification.

The slow saponification of the fat is accomplished by the use of sulphuric acid at a low temperature; the more sulphuric acid one employs, and the lower one keeps the temperature, the longer is the time required for the decomposition of the fat to be carried to completion, and a proportionately larger mass of fat is lost owing to further decomposition, both as regards production of fatty acids and of glycerine.

In the first instance, therefore, one employed as much as 37 per cent of sulphuric acid of the weight of fat, and completed the process by gently heating to 86-92° C. for twenty-four to thirty-six hours. Subsequently one proceeded with ever decreasing quantities of sulphuric acid, and raised the temperature to 100-120° C. in order to complete the reaction with the use of only 5½ per cent sulphuric acid in a period of twelve to eighteen hours. That the chemical process of saponification of fats with sulphuric acid, which theoretically takes place in a very simple manner, in practice is not by any means so simple, is proved by the behaviour of the heated mass. It evolves violet vapours, empyreumatic smelling oils, sulphurous acid, and vapours of acrolein in such considerable quantity that the decomposition vessel must be made absolutely closed, and an exit provided for the vapours evolved during the heating.

The vapours of acrolein are produced by the decomposition of glycerine; not only this, but the fatty acids are also attacked, and a black-coloured mass of a pitch-like nature is formed, which can be separated from the fatty acids only by distillation of the latter. The total loss which occurs in this process is very considerable, and may amount to 20 per cent of the fat employed; only in very rare cases is it less than 12 per cent.

After completing the saponification the mass is treated with boiling water to separate the fatty acids from the glycerine and sulphuric acid; the fatty acids are worked up further into pure stearic and palmitic acid, while the sulphuric acid and glycerine-containing liquid can be either worked up directly for glycerine, or can be turned to good account by using it for the decomposition of lime soap. One obtains then besides free fatty acids and gypsum a liquid which contains acid-free crude glycerine. For the method of quick saponification or fractional saponification one takes a small quantity of fat, raises its temperature to 90-120° C. and mixes thoroughly with sulphuric acid, leaves in contact during a short time—for a few minutes, or even half an hour—and then allows it to drop into boiling water; in this glycerine and sulphuric acid dissolve, whilst the fused fatty acids collect as an oily layer on the surface of the liquid. Working in this way it is sufficient to use 3½ to 4 per cent of sulphuric acid, and the reaction, which for its completion by the older process required many hours, is finished in a few minutes; one chief advantage of this process lies, however, in the fact that there is only a small loss by decomposition of fat and sulphuric acid; it evolves very little sulphurous acid, and an acrolein odour is scarcely perceptible.

In place of the sulphuric acid alone a mixture of sulphuric acid with nitric acid has also been used for the purpose, in order to prevent completely the formation of dark-coloured products which, when working with sulphuric acid alone are never quite avoided. The treatment of the fats with this acid mixture takes place at a temperature of 110-115° for a few minutes. There is employed to 1000 parts of fat 1-6 parts of nitro-sulphuric acid, and by this process also the glycerine is obtained in a completely unchanged condition.

Anhydrous zinc chloride effects decomposition in the same manner as acids, and one can carry out the decomposition rapidly by using 10-12 per cent of the weight of fat and a temperature of 150-

200° C.; the zinc chloride which has absorbed water can be again regenerated in the anhydrous condition, and the same mass of zinc chloride—of course making up the part missing through inevitable loss—may be used over and over again. In addition to the lower price of sulphuric acid, however, the regeneration of the anhydrous zinc chloride is accompanied by an expense which is higher than the cost of the sulphuric acid, for which reason this process has not found employment in practice.

THE TWITCHELL PROCESS

Although the sulphuric acid process is to-day employed only comparatively rarely, yet there results from this the Twitchell process, which is utilized especially for the production of fatty acids for soap manufacture. In this process there is used, instead of sulphuric acid, a combination of sulpho-oleic acid with naphthalene (D R P. 114, 491). The fat to be decomposed is heated to about 50° in a vat provided with an air-blast and steam coil, and mixed, with vigorous stirring, with 1·5 per cent sulphuric acid at 60° B. The addition of sulphuric acid, after the addition of which the agitator is kept going, has the object of purifying the fat by the destruction of albuminous and mucilaginous matter, and preparing it for the subsequent decomposition, but the acid employed should not be stronger than mentioned, because otherwise it attacks the fat itself and colours it brown.

The sulphuric acid, diluted by the condensed steam, is then drawn off, and the fat transferred to the splitting vat, where one mixes it with about 0·33 per cent of the previously mentioned combination of sulpho-oleic acid and naphthalene, adds 50 per cent water, and boils by introduction of steam. The splitting vat is made of pitch-pine wood; iron or lead would retard the decomposition. The conducting pipe for the steam is made of brass.

When the mass has boiled slowly for twenty-four hours, as a rule 85 per cent of the fat will be split. At this stage, in order to exclude the fatty acids from contact with air, whereby they become discoloured, one allows steam to blow on to the surface of the liquid. Then the mass is left at rest for the glycerine water to settle. This, the so-called "first water," is drained off, and fresh water added. The whole is then boiled further, with addition, if necessary, of a little more sulphuric acid, until in all 92-95 per cent of the fat is split, which requires as a rule a further twenty-four hours. For neutralization of the free sulphuric acid one utilizes barium carbonate, and after the settling of the barium sulphate, the fatty acids and glycerine water are drawn off.

3. DECOMPOSITION OF FATS BY STEAM.

When a fat is heated with steam under pressure to 220°, decomposition into free fatty acids and glycerine takes place. In practice, where this autoclave treatment is employed to a very considerable extent, one takes care, however, to accelerate this reaction by the use of assisting or catalytic agents. As such comes into consideration first lime and then magnesia.

The process of fat splitting by steam under pressure is carried out in special apparatus, the autoclave, which sustains a pressure of 12-15 atmospheres, and therefore must be tested at a higher pressure. The fat splitting takes place in the beginning moderately quickly, so that perhaps after expiration of an hour, already 85 per cent of the fat will be decomposed. Then the reaction slackens itself, however, and in order that the heating may not be unduly prolonged, one has recourse frequently to the expedient of not carrying the splitting quite to completion in the autoclave, but to split the rest of the neutral fat by treatment in the acidificator with concentrated sulphuric acid. This treatment possesses especial importance for the stearine manufacturer, since during the treatment with concentrated sulphuric acid, a simultaneous transformation of the oleic acid takes place, isoleic acid being produced. This is solid, and consequently the yield of fatty acid suitable for candle manufacture is materially raised. Of course the fatty acids are dark coloured after the acidification, due to decomposition products; they are therefore washed with water, and subjected to distillation.

The process of fat-splitting is different in general, according as it is carried out for stearine or soap manufacture. In the first case tallow is mostly employed, then bone fat and palm oil. The fats are first of all subjected to a refining process, in order to separate albuminous matter, etc., and are then introduced into the autoclave where they are treated, with addition of magnesia (0·5 to 1 per cent), during six to eight hours, under a pressure of 12-15 atmospheres. A decomposition of up to 95 per cent is thereby obtained, after which follows the previously described acidification

The course of the decomposition is shown in the following table by B Lach, which indicates how the process gradually becomes slower

The mass contains

After	1 hour	35·5	per cent	free	fatty acids.
,,	2 hours	76·0	,,	,,	,,
,,	3 ,,	77·4	,,	,,	,,
,,	4 ,,	84·7	,,	,,	,,
,,	5 ,,	88·6	,,	,,	,,
,,	6 ,,	90·8	,,	,,	,,
,,	7 ,,	94·0	,,	,,	,,
,,	8 ,,	97·4	,,	,,	,,
,,	9 ,,	97·9	,,	,,	,,
,,	10 ,,	99·1	,,	,,	,,
,,	12 ,,	99·3	,,	,,	,,

4. DECOMPOSITION OF FATS BY ENZYMES.

Besides the substances already mentioned—alkalies, sulphuric acid and steam under pressure—the decomposition of fats into fatty acids and glycerine can also be effected by means of other agents. For this purpose are particularly useful certain enzymes which are found in the seeds of many plants, especially in castor seeds, and during the last few years the enzyme or fermentation process of fat-splitting has attained considerable importance. The process is quite analogous to that with sulphuric acid or steam, and as with these two latter reagents, so the enzyme does not take any active part in the reaction, but acts rather by its mere presence, so that its mass and substance remain unchanged. Theoretically, therefore, only quite a small quantity should be able to split an infinitely large mass of fat. In practice, however, one always takes a considerably larger quantity, in order to produce a certain reaction velocity.

Originally merely crushed or ground castor seeds were employed for the fermentation fat-splitting process, but it has been found that the use of an extract is far more suitable for the purpose. A peculiarity of all enzymes is that they are only active within certain fixed limits of temperature. Below the most favourable temperature the action is always slower and more feeble, though by raising the temperature to that most suitable the activity is restored, and consequently has not been destroyed by the cold. When the best temperature is exceeded, a slackening of the action also occurs, while at a certain temperature, most undoubtedly at 70°, the enzyme completely loses its activity, and is destroyed.

The enzyme method of fat-splitting is carried out by melting the fat in a pan with a conical bottom and fitted with a steam coil, the temperature not being raised too high, since the best temperature for the ferment action lies between 25 and 35°, while above 40° it is very considerably reduced. The molten fat is kept at about 30°, mixed with about half its weight of water, and a small quantity of castor seed extract added, whereupon the whole is thoroughly mixed. It forms a thick emulsion, in which the splitting of the fat slowly takes place. It is mostly ended after six or eight hours, when some 80-86 per cent of the fat will be decomposed. The addition of manganese sulphate hastens the decomposition.

At the end of the time during which the enzyme is allowed to act on the fat, the mass is heated to 100° to kill the enzyme, after which the mass is allowed to rest. It settles into three layers, the top one being the pure fatty acids, the middle one an emulsion of fatty acids and ferment, this being considerable when one uses merely crushed castor seeds instead of the castor seed extract. The bottom layer consists of the glycerine water. All three layers are then further dealt with.

THE NATURE OF GLYCERINE WATER

By employing one of the above-mentioned processes for the decomposition of fats, one always obtains liquids in which, besides water, larger or smaller quantities of glycerine are present. In addition to these two bodies there are also found in the liquid all those substances which were admixed with the original fat employed, or were introduced during the saponification or process of decomposition. The raw glycerine liquor therefore in most cases possesses an evil, often very disagreeable odour, and a yellow-brown to dark-brown colour.

The liquid which is obtained by the decomposition of lime soap with sulphuric acid, has always a considerable quantity of calcium sulphate (gypsum) in solution, since the gypsum which is only slightly soluble in water dissolves much more easily in a liquid containing glycerine than in water. This solubility of calcium sulphate renders it difficult to produce a glycerine quite free from lime from a glycerine water produced by the decomposition of lime soap.

If the saponification of the fat is carried out under high pressure, so that one uses, as has already been mentioned, a very small quantity of lime or magnesia, it is then easier to produce from the lyes which are yielded by the decomposition of the lime soap a glycerine which will contain only a very small quantity of lime. Absolutely lime-free glycerine, however, is scarcely obtainable in this way.

By the saponification of fats with sulphuric acid—if one does not work according to the quick saponification process—a very large part of the glycerine present is completely lost, owing to its decomposition; the raw glycerine obtained is very dark brown owing to the numerous decomposition-products which are dissolved in it, occasionally quite black, and it is very difficult to produce from raw glycerine which has been obtained by the slow saponification with sulphuric acid a product free from colour and odour. In any case the cost of this is so high that one usually does not attempt to produce a first-class product from such glycerine, but rather sells it in a not quite pure state.

The best yield of fatty acids, as also of glycerine, both in regard to quantity and quality, is obtained by saponification with steam under high pressure. In addition, this process is extremely simple and costs little, so that it must be described as that which above all others is to be preferred. For this reason, the largest stearine and glycerine works at the present time work exclusively according to the process of saponification with steam, and it is really through the employment of this process that the production of almost chemically pure glycerine, in any desired quantity, first became possible.

5. RECOVERY OF GLYCERINE FROM SOAP LYES.

The saponification process takes place, so far as the substances arising therefrom are concerned, always in the same way: there is formed a combination of the fatty acids with a basic substance (potash, soda, lime, etc.), while the glycerine is liberated in the free state. Glycerine, therefore, is always produced as a by-product in the manufacture of soap.

The production of soap is carried out, as is well known, in small soap works by boiling the fat with potash lye until saponification is complete, and the potash soap so formed, which because of its lack of firmness is not well suited for many purposes, is then converted into sodium soap. This is effected by adding common salt to the potash soap, whereby double decomposition takes place in such a way that sodium soap is formed, and potassium chloride goes into solution. The soaps are, with the exception of that produced from coconut oil, insoluble in brine, and are therefore separated out by addition of an excess of salt, or, as the technical expression has it, salted or grained out.

In the larger soap works, one saponifies direct with soda lye, and sometimes carries out the graining out not with common salt, but by addition of very concentrated caustic lye, which likewise causes the separation of the soap. In the stearic acid factory, finally, one manufactures the oleic acid, obtained by pressure of the fatty acid mass, directly into soap by boiling it with caustic lye.

The waste lye from the manufacture of soap, according to the old processes, contains potassium chloride or sodium chloride, and excess of free alkali in addition to glycerine, and can be employed under favourable circumstances for the production of the latter. Formerly this production was actually carried out, but in a rather unsatisfactory way, the excess of free alkali in the lyes being exactly neutralized with hydrochloric acid, and the liquor allowed to evaporate on the water-bath. There was formed in this way a mass of salt, which always remained sticky on account of the glycerine admixed with it.

This salt mass was treated with strong (90 per cent) alcohol, which brings into solution only very little of the salt, but very easily the whole quantity of the glycerine. The solution separated from the salt mass was freed from alcohol by warming up to 100° C. in a distillation plant, and one obtained as residue in the retort a syrupy liquid of yellow to brown colour—impure glycerine.

Glycerine may be recovered from the lyes of the soap boiler in a less costly way, by evaporating the neutralized lyes in shallow open pans over a fire until its boiling-point reaches 109° C., like the boiling-point of a concentrated solution of common salt. The neutralization is absolutely necessary, and indeed is so carried out that neither an excess of alkali nor acid remains in the liquid, as the presence of either causes the glycerine to be badly contaminated by the formation of decomposition products.

During the evaporation, salt continuously separates out from the liquid, and this is removed by means of suitably formed rakes at the edge of the pan, lifted up and brought into a basket which hangs over the pan, so that the liquid mixed with the salt can drop back again into the pan.

The temperature of 109° C. is finally reached, when one allows the liquid to run off into a distillation apparatus, in which it is further concentrated, until the thermometer, which is immersed in the liquid, reaches exactly 193° C.; the heating by fire is then stopped, and a stream of superheated steam led through the liquid, the flow of steam being so regulated that the temperature does not fall below 193° C., and does not rise much above this point, as in the first case no glycerine would distil over, and in the other case the glycerine might be contaminated with acrolein.

The lyes of the soapmaker contain 0.92-1.8 per cent of glycerine.[1] One cools it thoroughly, filters to remove suspended matter, evaporates it up to a glycerine content of 10 per cent, acidifies with hydrochloric acid, filters, concentrates it in vacuo up to 80 per cent, cools thoroughly, and filters. This crude glycerine is distilled in vacuo. The portion passing over between 170 and 180 is once-distilled glycerine of commerce; by repeated distillation it furnishes pure glycerine. Or one mixes the lye with sulphuric acid, filters, evaporates in vacuo up to 22° B., then in another apparatus to 28° B., whereupon most of the common salt separates, and can again be used for the salting out of soap. The glycerine is distilled in vacuo, then concentrated in vacuo up to a specific gravity of 1.263, once more distilled and concentrated, and finally decolorized with animal charcoal.

The evaporation apparatus which one uses for the concentration of the lyes are so constructed that under them are cylindrical vessels with sieve bottoms. These salt-boxes are during the evaporation combined with the upper part of the evaporator, so that the salt separating during the evaporation falls into the box and collects on the sieve. When the box is almost filled with salt, which can be ascertained through spy-holes, one shuts the connexion between it and the evaporator, and establishes only a connexion between this and the part of the box to be found under the sieve-bottom. The vacuum prevailing in the evaporator is thus transmitted thither. If one now allows air to pass into the upper part of the box, then the atmospheric pressure forces the liquid contained in the salt along, and finally into the evaporation apparatus, whereupon one covers yet with steam, in order to obtain all the glycerine out of the salt.

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[1] *Translator's note.* — It is frequently higher in this country, and may reach as much as 7 per cent.

The salt mass one brings finally into a centrifuge, where it is extracted with water until it only contains 0·25 per cent glycerine. With the help of this apparatus, one is able to produce from lyes crude glycerine of 80-84 per cent glycerol and 9-10 per cent ash.

CHAPTER IV

THE PRODUCTION OF PURE GLYCERINE.

When it was commenced to produce glycerine on a large scale, one had to contend with innumerable difficulties in order to obtain a product which was not only colourless and brilliant, but also odourless. The absence of odour was especially difficult to obtain, and it was consequently attempted to perfume the really evil-smelling glycerine: it owes this unpleasant smell to the admixture of a small quantity of acrolein. For the expert, however, no deception was possible, because the smell of acrolein is so characteristic that it stands out clearly above any other smell which is intended to mask it.

It was early tried to concentrate glycerine by evaporation until it began to distil, and the distillation then carried on in closed vessels (stills). But though one proceeded cautiously in this way with the distillation, it was yet, and especially towards the end of the operation, almost impossible to avoid the formation of a small quantity of acrolein.

It was further sought to obtain the glycerine water clear and at the same time free from odorous substances by means of filtration through bone-charcoal; this accomplishes the first, but not the second, object, and the glycerine absorbs, in consequence of its large solvent power for lime salts, considerable quantities of these out of the bone-charcoal.

It was not until the introduction of aqueous saponification that the perfecting of the production of pure glycerine on a manufacturing scale was satisfactorily accomplished so that there is in existence in commerce true glycerine, which can be regarded as chemically pure and consists really only of glycerine and water.

The employment of absolutely pure fats may be regarded as the main condition for the production of pure glycerine in this way, because otherwise the foreign matters remain behind in the glycerine solution, and cannot be quite completely removed from it. The fats to be employed therefore more especially in the case of animal tallow must, before they are ready for saponification, be purified with the utmost care, and this is accomplished by treatment of the same with very dilute sulphuric acid or soda lye, with simultaneous heating. All membranous parts, which are mixed with the tallow, are thereby destroyed, and the decomposition products arising dissolve in the acid or alkaline liquid, on which finally floats the pure melted fat, which is either moulded into blocks, or immediately brought into the decomposition vessel.

The decomposition of the fats is completely effected in this decomposition apparatus, and with the employment of the smallest possible quantity of water, so one obtains immediately a very pure crude glycerine, which only needs to be refined and evaporated with suitable precautions in order to give after distillation pure highly concentrated glycerine.

The removal of these foreign, contaminating substances is also necessary on this account, that it would give rise to the most objectionable foaming during the subsequent manufacture. The contamination consists, according to the origin of the glycerine water, of soap, fatty acids, albuminous matter, etc. One removes these substances by boiling up, neutralising, and subsequent treatment with sulphuric acid, whereupon one filters. The glycerine so purified is then concentrated in the vacuum apparatus. Quite pure glycerine should be obtained, which is steam distilled in vacuo.

THE DISTILLATION OF GLYCERINE.

If one concentrates and finally distils glycerine over an open fire, it is not possible to prevent a part of the wall of the still becoming heated above the boiling-point of the glycerine, and the glycerine vapour coming into contact with it yields a small quantity of acrolein. In order to avoid this defect heating with an open fire has been quite given up, and in its stead heating with superheated steam introduced, the steam being passed direct into the glycerine.

So long as excess of water is contained in the glycerine, one can allow the steam to enter the liquid at a temperature of 300° C. and more, it then only evaporates water. When, however, the temperature in the distillation apparatus reaches 280° C. the glycerine itself begins to boil, and now the greatest attention must be given to the regulation of the steam; one adjusts it in such a way that the temperature remains constant between 280° and 290° C. The glycerine distils then in the steam without any decomposition and passes over quite uniformly. Instead of effecting the concentration by directly introducing superheated steam, one also occasionally finds a steam coil inserted in the distillation apparatus, through which one first allows to pass ordinary steam at 3-4 atmospheres pressure, shutting this off as soon as the temperature in the still has become similar to that of the steam. One then allows immediately after shutting off the ordinary steam, superheated steam to pass until the temperature of 280° C. is reached, when one also shuts off this steam and henceforth allows superheated steam to pass directly into the contents of the still for the real distillation of the glycerine.

The cooling of the vapours takes place in a condenser of unusual construction, the respective apparatus being arranged in the following manner.

The copper coils, six in number, lie in a plane parallel with each other at the bottom of a tank, which is fed continuously with cold water, and are at the ends bound together with curved blocks. To each of these curved ends is fixed a tube which goes vertically downwards through the bottom of the cooling vessel, and underneath the same is bent in the form of a U (siphon-shaped). Under each of these tubes is placed a vessel for the reception of the glycerine.

The glycerine vapours are so much the less volatile, as they contain less water, and consequently the condensation takes place in the following way: the glycerine most free from water condenses in the first of the condensing tubes and flows off through the first U tube; afterwards the vapours are passed through a second tube, where condenses a glycerine already rich in water, which runs off through the second siphon tube, etc., until finally only pure water flows out from the last tube.

An apparatus of this kind, but of newer construction, is shown in Fig. 1 (according to Ubbelohde). The retort A, made of copper, wrought iron, or cast iron, has at its base a draw-off cock B, through which, after termination of the distillation, the residue is withdrawn. Into the still passes, through the tube F, steam from the steam superheater D. It enters through the steam distributor G into the glycerine, which passes into the still from the reservoir H through the cock and tube J. For the control of the temperature in the still and of the superheated steam the thermometers K and E are used.

The vapours escaping from the still through the neck L are first of all usefully employed to warm the glycerine in H. Hereby is already condensed a part of the vapour which is withdrawn at M. The vapours reach several cooling tubes, standing side by side, and made of copper, from whose under ends the condensed liquid can be drawn off through the siphon-shaped bent tubes. Those vapours, which have passed even through the last cooler uncondensed are still further cooled by means of cold water. The distillate collected in the last of these coolers consists then merely of water.

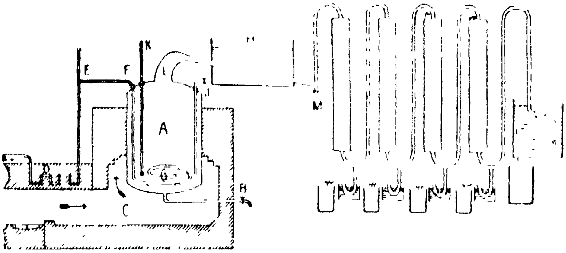

FIG. 1.

The temperature of the entering steam reaches mostly 260-290, the temperature in the still 200-220. The glycerine which is obtained from the first receiver contains only about 10 per cent water, corresponding to 28 B. In the following receivers collects more and more dilute glycerine. The distillation proceeds continuously, glycerine flowing out of H into the mass as it evaporates. Finally, however, there collects a large mass of non-volatile residue in the still which is decomposed by heat, and contaminates the distillate. Acrolein is formed, and further, the glycerine becomes coloured yellow.

When this point is reached one shuts off the inflow of glycerine and distils the contents of the still to the end, and then collects the distillate separately.

Finally the distillate is concentrated in vacuum apparatus, and if quite pure glycerine is to be produced once more distilled in vacuo

As described here the distillation takes place under the ordinary atmospheric pressure, a proceeding which is attended with certain inconveniences. One employs therefore mostly distillation in chambers under reduced pressure, whereby one can distil at lower temperatures and obtain a purer product of higher concentration

As is well known the boiling-point of a liquid depends on the superincumbent pressure, and becomes so much the lower as one reduces the pressure. This law of nature has long since been made use of in the manufacture of substances which are easily decomposed at high temperatures: in sugar factories, for example, the evaporation of the sugar solutions takes place exclusively in the so-called vacuum apparatus, in which through exhaustion of the air, and continuous condensation of the escaping water vapour, very low pressure is obtained.

In order to obtain glycerine by distillation completely colourless and free from any smell, the distillation apparatus has been constructed of a similar type, so that the distillation of the glycerine takes place under reduced pressure.

The head of the still is, for this purpose, fitted perfectly airtight on to the still, and also connected with an airtight joint to the condensing plant; the tubes fixed to the still head and leading downwards are in this case, however, straight, and the vessels which serve for the collection of the glycerine flowing out of these tubes are also fitted airtight with them. The end of the cooling tubes is connected with a double air-pump of suitable size and with the receiver for the condensed liquid.

As soon as the distillation vessel is filled up to a suitable height with the crude glycerine, one sets the air-pump in action, then allows steam to enter, and accomplishes the distillation under the continuous action of the air pump in a shorter time, and at a much lower temperature than that at which glycerine boils under ordinary atmospheric pressure.

Whilst at the ordinary atmospheric pressure (760 mm. mercury) the glycerine boils constantly at 290° C., boiling takes place at a pressure of 500 mm. mercury, already at 210° C.; when one has a pressure of only 12.5 mm., then glycerine boils at 179.5°, and it is therefore advisable to provide the distillation apparatus with a very strongly acting air-pump, so that a very low pressure can be obtained. By adequate influx of steam the boiling then takes place very quickly, and the distillation is completed in a very short time.

The apparatus of Heckmann (Fig. 2, after Ubbelohde) illustrates the principle of this apparatus (D.R.P. 6517). The glycerine to be distilled is placed in a walled in still A, into which superheated steam at 200-300° C. is introduced. The glycerine vapour

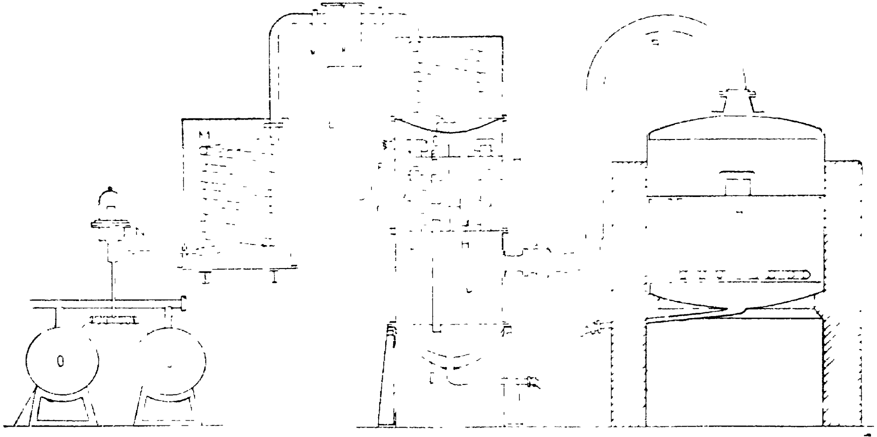

Fig. 2

passes over through the tube B into the cooling receiver C, which is of similar construction to the tower of an alcohol-rectifying apparatus. It is provided with a heating arrangement D in order to maintain the temperature at about 80, so that the water present in the condensed glycerine is caused to evaporate. The vapours rise through a number of stories E, which are arranged over C, and with breaks at F, which allow of the passage through of the vapours. Covers G and overflow tubes H are provided, through which must run the glycerine-containing liquid collecting in any single story, whilst this runs downward through the overflow tube from one story to the other. In this way the liquid always comes again into contact with the hot vapour streaming in, whereby it becomes the stronger in glycerine the more it approaches C. Finally the hitherto uncondensed vapours proceed thence into the condenser J, which is cooled with just sufficient water, so that only little water but all the glycerine is completely condensed, and proceeds back into the story E. In order that the condensation of the glycerine may be complete one employs further a condensing arrangement K, from which through L the condensed liquid passes likewise to E. The vapours now freed from glycerine are finally condensed completely in M. The condensed liquid, consisting almost entirely of water, passes through the gauge N into the collecting vessel O, to which a powerful air-pump is connected. The water removed by means of the gauge should test at the most 1 Be. A higher concentration would indicate that the condensation is not taking place properly, and too much glycerine is passing over

Varying from the above description is the apparatus for the distillation of crude glycerine constructed by Van Ruymbeke and W. F. Jobbins (D R P. 86,829). In order to avoid any decomposition of glycerine which the use of superheated steam brings about, and loss of heat through the expansion of the steam introduced into the still, and also to prevent the slackening of distillation through the steam condensing in the boiler, the inventor allows the steam to expand in a coil enclosed in a hot vessel, whence it first enters the still.

In practice the Ruymbeke apparatus has proved very good, since it presents many advantages over the apparatus of the older systems One such is that it can be employed as well for the distillation of saponification as of soap-lye glycerine

THE FILTRATION OF GLYCERINE.

In addition to distilled glycerines, refined glycerines which have only been bleached by bone-charcoal are also used in commerce. For this purpose they are diluted to 50 per cent with water and passed through a filter battery.

As bleaching material bone-charcoal or spodium may be used, which not only extracts the colouring but also any odorous substances; as, however, as already indicated, glycerine possesses a strong solvent action on salts of lime, it becomes colourless and bright after filtration, but it has dissolved salts of lime from the bone-charcoal, and in order that these may be removed it must be delimed.

Filtration of glycerine is a very lengthy operation, and to ensure a regular course of work it is absolutely necessary to have a sufficient number of charcoal filters ready, and so to combine them in batteries that the amount of glycerine placed on the first filter, after it has passed through one or several batteries, should flow out of the last filter as a perfectly clear and bright glycerine. With regard to their disposition the filters used for filtration of glycerine are very similar to those used for the purification of sugar solutions in sugar factories.

As the absorption power of bone charcoal for colouring and odorous substances is not unlimited, the filters must be renewed from time to time. As a rule, the filter batteries are placed together in such a manner that, for instance, six filters are connected with one another; the first filter through which the glycerine flows will also be the first to become ineffectual as it will have already extracted from the glycerine large quantities of colouring and odorous substances. This filter is then removed, and at the end of the battery a filter filled with fresh bone-charcoal is placed, so that now the filter which was No. 2 is No. 1 and No. 6 is No. 5. No. 6 is the newly added filter.

The porous bone-charcoal retains considerable quantities of glycerine, and this glycerine can be obtained by forcing it out with water which is let flow into the filter. The glycerine is somewhat diluted by this process, and for subsequent distillation it is mixed with other fresh material.

Bone-charcoal which can absorb no more substances from the glycerine is revivified in a similar manner to that adopted in sugar factories. The charcoal is washed and the washing water can again be used for dilution of the glycerine in order by this process to obtain the small quantities of glycerine contained therein. This washed bone-charcoal is treated with hydrochloric acid and soda lye, dried and heated to redness in closed vessels, whereby the organic matter absorbed by the charcoal is destroyed, and it can then again be utilized for the decolorizing of more glycerine.

If ordinary bone-charcoal is used for the filtration of glycerine, salts of lime are dissolved from the charcoal, which in some cases in which glycerine is used, are of no importance; glycerine which is used for certain, notably medicinal purposes should, on evaporation, leave no residue and, therefore, it should be delimed and again distilled.

In order to avoid the formation of any colouring matter, this distillation should be proceeded with in the most careful manner with regard to temperature, and 290° C., the actual boiling-point of glycerine, should not be reached, but the addition of steam should be so controlled that distillation should take place at 287°-289° C., and particularly in the case of this latter distillation the application of reduced pressure is of the greatest advantage, inasmuch as the risk of the formation of colouring substances is decreased the lower the temperature at which distillation takes place.

The filtration of glycerine over bone-charcoal is a very lengthy and tedious operation, therefore decoloration is also carried out by heating the raw glycerine to 100 by steaming it in a boiler fitted with a stirring device, adding a bleaching agent, such as black spodium powder, etc., and then carefully stirring it. Generally 3-15 per cent bleaching material suffices, and within one to a couple of hours sufficiently thorough bleaching is obtained. This has the further advantage that the glycerine then only absorbs very small quantities of lime from the charcoal, so that subsequent deliming can be dispensed with. In the case of glycerine bleached in the batteries already mentioned, however, deliming is absolutely necessary. The bleached glycerine is finally placed in a vacuum apparatus and brought to the requisite concentration.

Deliming of glycerine can be carried out in such a manner that the dissolved lime is converted into an insoluble compound which can be removed by filtration. To this end sodium carbonate, sodium oxalate, or acid sodium phosphate is added to the heated glycerine, which causes the formation of insoluble calcium carbonate, oxalate, or phosphate.

PURIFICATION OF GLYCERINE BY MEANS OF CRYSTALLIZATION.

Glycerine possesses the quality of crystallizing at a low temperature, and by this process a product of considerable purity can be obtained from fairly impure glycerine. The discovery of this crystallizing property of glycerine was a mere chance; in the winter of 1867 the large stearin and glycerine factory of Sarg & Co., at Liesing near Vienna, shipped a number of casks containing glycerine to England, and one of the casks arrived with the contents so completely crystallized that it had to be chiselled out of the cask. In 1870 Kraut in Hanover invented a process by means of which glycerine of every quality and in large quantities can be crystallized; this process is still sometimes used.

Crystallization takes place in leaden vessels, the mother liquor is poured off after crystallization, and the crystals are freed from any of the mother liquor by being swirled round in a very rapidly rotating centrifugal machine. On melting these crystals at +18 to +20° C., very pure and colourless glycerine is at once obtained.

CHAPTER V

THE PROPERTIES OF GLYCERINE.

The glycerine used in commerce, apart from its water content, which according to the variety generally fluctuates between 2 and 12 per cent. is practically chemically pure and can be obtained entirely free from water if it be left for a few days in flat dishes over concentrated sulphuric acid.

Glycerine free from water is a liquid as clear as water, of remarkably strong light-refracting properties and of a syrup-like consistency without any smell whatever and of an intensive burning sweet taste; in the mouth as well as on the skin of the body it causes a strong sensation of warmth, because it absorbs water very powerfully. Exposed to the air, all concentrated glycerine absorbs a great deal of water therefrom, and further absorption only ceases when the water content of glycerine has risen to about 50 per cent. The specific gravity of glycerine is 1·264 and decreases when water is added. The table given below shows the relation between the water content of the glycerine and the specific gravity of the product in question, and, therefore, when using these tables a simple determination of the specific gravity by means of an ordinary hydrometer is sufficient in order to obtain at once the percentage of glycerine.

On cooling below the freezing point of water, the glycerine congeals to a crystalline mass and forms monoclinic crystals the size of a pea, of diamond like brilliance, particularly if crystallisation is stimulated by introduction of a crystal. The crystals melt at + 17° and glycerine which has crystallised and then been melted again, is said to remain liquid for half an hour even after cooling to –20° C.

The freezing-point of glycerine diluted with water depends on the water content. The following table gives the specific gravity of aqueous glycerine solutions determined at 15° and the freezing points :—

Specific Gravity at 15° C.	Glycerine	Freezing-Point
1·021	10	1
1·051	20	2·5
1·075	30	6
1·105	40	17·5
1·127	50	21–34
1·159	60	
1·179	70	below 35
1·204	80	
1·232	90	
1·241	94	

If quite colourless glycerine is heated in open vessels, then after a time it becomes yellow and can be heated to 120° C. without changing any further; at this temperature it begins to give off fumes which smell like boiling glue; at a temperature of 290° it boils; if the experiment is carried out in glass vessels, these should be placed on a sand-bath, as the glycerine boils so powerfully that an unprotected vessel would easily break.

Glycerine evaporates noticeably at 100°, particularly with water-vapour. In a sufficiently fine state of division it vaporizes even at the ordinary temperature. In spite of this it is to be considered as a non-volatile liquid which also does not change in the air. Important is the property of glycerine that under reduced pressure it can be distilled with steam at temperatures of 180°-200° without decomposition.

If glycerine be heated to 150°, it easily takes fire and burns with a steady blue flame to carbonic acid and water without developing any smell; a wick is not necessary for this purpose.

Glycerine is very hygroscopic, that is, it absorbs water from the air, and if fully concentrated glycerine be used it absorbs its own weight. With water, alcohol, and ether-alcohol, with concentrated sulphuric acid, and caustic lye it can be mixed in all proportions, but not with ether, chloroform, benzine, and fatty oils. It dissolves alkalies and alkaline earths, lead, copper, and iron oxide, as well as many salts and alkaloids.

Glycerine prevents the precipitation of the heavy metals by alkalies. Whereas, for instance, caustic lye at once precipitates voluminous copper hydroxide from a solution of chloride of copper, this does not take place on boiling if glycerine be added. Fused with potassium hydroxide, glycerine gives acetic acid, formic acid, and hydrogen; heated with phosphorus pentoxide or with sulphuric acid it gives acrolein. If a mixture of glycerine and oxalic acid be distilled, the glycerine remains unchanged, but the oxalic acid is split up into formic acid and carbonic acid. If the mixture is heated to over 100°, allyl alcohol is produced.

By means of diluted nitric acid glycerine is oxidized to glyceric acid and glycollic acid; if the oxidization process is gentle, glycerose is formed, consisting principally of glyceric aldehyde, and dioxyaceton. Concentrated nitric acid oxidizes it to oxalic acid and carbonic acid. Phosphorus iodide forms allyl iodide from which essential oil of mustard (allyl sulphocyanide) and garlic oil (allyl sulphide) can be obtained.

If water-free glycerine is placed on the skin it causes a burning sensation owing to the extraction of water. Administered internally 10-15 grammes suitably diluted has no effect, larger quantities have a purgative action. In the organism the glycerine is partly combusted and partly separated again without any modification. Introduced into the blood, large quantities have a poisonous effect on the central nervous system, the intestines, and the kidneys.

If glycerine is boiled in open vessels it gets darker, and in addition to glycerine vapours it evolves products of decomposition which have a very unpleasant smell, and in which are present, besides acrolein, acetic acid and other acids of the fatty acid series. Finally, there remains a mass which becomes darker and darker and is reduced to ashes by strongly heating. Glycerine can be distilled without alteration only in a vacuum chamber and by means of a stream of super-heated steam.

Glycerine is characterized by its property of dissolving a large number of substances which otherwise would only be dissolved with difficulty, and for this reason it is used in many branches of technical chemistry. It is largely used in the manufacture of perfumes and soaps, further in dyeing works and also in medicine as a solvent. We give below some indications as to the solubility of different substances in glycerine. 100 parts of glycerine dissolve 98 parts of crystallized sodium carbonate, 60 parts of crystallized borax, 50 parts of chloride of zinc, 10 parts of alum, 10 parts of potassium iodide (according to Farlay, however, only 1 part of potassium iodide can be dissolved in 3 parts of glycerine), 33 parts of potassium cyanide, 30 parts of ferrous sulphate, 30 parts of copper sulphate, 20 parts of sugar of lead, 20 parts of ammonium carbonate, 20 parts of sal ammoniac, 10 parts of barium chloride, 8 parts of sodium sesquicarbonate, 7·5 parts of chloride of mercury, 3·5 parts of potassium chlorate. Further, 2000 parts of glycerine dissolve 1 part of sulphur, and glycerine is also an excellent solvent for salicylic acid, for aniline dyes, etc. Further 1 part of iodine can be dissolved in 100 parts of glycerine, mercury iodide in 340 parts, quinine sulphate in 18 parts, tannin in 6 parts, veratrine in 96 parts, atropine in 50 parts, morphine hydrochloride in 19 parts, tartar emetic in 50 parts, and potassium sulphide in 10 parts of glycerine.

Glycerine itself is miscible in all proportions with water and alcohol or with a mixture of alcohol and ether, but insoluble in pure ether, benzol, carbon bisulphide, and chloroform.

CHAPTER VI

NITRO-GLYCERINE

PROPERTIES OF NITRO-GLYCERINE

As early as 1847 the combination known under this designation was produced by treating glycerine with nitric acid, and its explosive qualities were also recognized. This combination was also called pyro-glycerine as a reminder of its analogy with pyroxylin or gun cotton which also possesses the property of exploding violently.

The explosive qualities of nitrated glycerine, however, remained totally ignored until 1863, when the Swede, Nobel, applied it to the science of blasting. The so-called Nobel explosive oil is nothing but nitro-glycerine, and to Nobel, though he did not discover it, must be attributed the merit of having produced it on a large scale and applied it as an explosive

The actual application of this oil as an explosive dates, however, only from that period (1867) when it was possible to produce it in such a form that the handling of this substance was no longer accompanied with such great risk as in the case of the explosive oil pure and simple.

The chemical constitution of nitro-glycerine has already been set forth; it is not a nitro-compound in the sense, for instance, that gun cotton and tri-nitro-phenol are, in which actually hydrogen is replaced by the radicle nitryl (NO_2), but nitro-glycerine is in reality an ester of nitric acid, in the same manner as in glycerine $C_3H_5(OH)_3$ the three hydrogen atoms of the hydroxyl groups (OH) can be replaced by acid radicles, so it is possible to replace them by nitric acid, and accordingly there is also a mono-, di-, and tri-nitro-glycerine, that is compounds in which one, two, or three atoms of hydrogen have been replaced in the three hydroxyl (OH) groups by nitryl (NO_2).

By treating glycerine with nitric acid all the three possible nitro-glycerines are obtained, the formulæ of which are as follows

$C_3H_5(OH)_2(O . NO_2)$ = mono-nitro-glycerine
$C_3H_5(OH)(O . NO_2)_2$ = di-nitro-glycerine
$C_3H_5(O . NO_2)_3$ = tri-nitro-glycerine.

For explosive purposes, tri-nitro-glycerine is the most important, and care must be taken to manufacture this product only. If nitric acid in a concentrated form is allowed to act on water-free glycerine, then at the commencement only tri-nitro-glycerine is formed, but on continuation of the reaction di- and mono-nitro-glycerines are formed as the nitric acid is diluted by the water which separates.

$$\underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{nitric acid}}{3HNO_3}$$
$$= \underset{\text{tri-nitro-glycerine}}{C_3H_5(ONO_2)_3} + \underset{\text{water.}}{3H_2O}$$

Therefore, in order to prevent as far as possible in the action of nitric acid on glycerine the formation of mono- and di-nitro-glycerine, care must be taken to remove the freshly formed water as soon as possible, and this can be done by mixing the nitric acid with concentrated sulphuric acid. The resulting water is at once bound by the sulphuric acid, and during the whole process the nitric acid keeps the necessary high concentration.

PRODUCTION OF NITRO-GLYCERINE ACCORDING TO SOBRERO

The oldest known process for the production of nitro-glycerine as indicated by the inventor of this compound is as follows: 2 parts of sulphuric acid of 1.831 specific gravity are mixed with 1 part of nitric acid of 1.525 specific gravity, and the mixture is left or placed in cold water until it has cooled to the ordinary temperature. Into the mixture a thin stream of half a part of highly concentrated glycerine is poured, and the liquids are mixed by stirring. Fairly strong heating results, and on treating large quantities of the material it is absolutely necessary to cool the vessel, which is most simply accomplished by placing in cold water.

The action of the highly concentrated nitric acid on the glycerine takes place in a very short time, and the liquid becomes turbid on the separation of the nitro glycerine, which floats about in fine drops.

As soon as an oily substance begins to detach itself from the acid mixture, the contents of the vessel are poured into a large amount of water which should amount to at least fifteen times that of the liquid contained in the nitrating vessels, and then the nitro glycerine which is specifically heavier than water settles at the bottom of the vessel. The acid liquid is drawn off, the nitro-glycerine repeatedly washed with water, and finally dried over sulphuric acid under an air-pump.

According to Sobrero's process, a very pure preparation can be obtained, the explosive action of which is all that can be desired; but the process in the form described is more suitable for laboratory experiment than for the production of nitro-glycerine on a large scale. In this case it is far more necessary to take certain precautionary measures in order to render the production of a substance such as nitro-glycerine, which has such terrible effects on exploding, as little fraught with danger as possible.

PRODUCTION OF NITRO GLYCERINE ACCORDING TO NOBEL.

Nobel, who as already stated may be looked upon almost as the second discoverer of nitro glycerine, but who, however, was the first to make practical use of this substance in connexion with explosives, succeeded in inventing a process by means of which large quantities of nitro glycerine can be obtained. Nobel's process at first was as follows:—

The nitration mixture was composed of dry saltpetre and sulphuric acid, and in such a measure that 1 part of finely powdered saltpetre was mixed with 3·5 parts of sulphuric acid, and the mixture cooled to 0° C., when by far the largest portion of the potassium hydrogen sulphate $KHSO_4$ crystallized out, and a liquid was obtained which consisted of highly concentrated nitric acid mixed with sulphuric acid. When this acid potassium sulphate had crystallized, the liquid was run off from the crystalline mass, and the glycerine poured into it; the formation of the nitro-compound quickly took place, and then the entire liquid was poured into water, when the nitro-glycerine was washed free from the acids attached to it and dried. At the time when the manufacture of nitro-glycerine was introduced, the daily press often reported on explosions which had taken place in the nitro-glycerine works, and the unexaggerated descriptions of havoc wrought by these explosions of large quantities of nitro-glycerine were ghastly enough to make the production of nitro-glycerine appear to be one of the most dangerous operations known. The reason of the frequent accidents caused by explosions in the nitro-glycerine works at first is not attributable to the easy disintegration of the nitro-glycerine itself, for this is rather a substance which only explodes by means of the application of certain special treatment, and which of itself could never explode spontaneously, that is by sudden disintegration without any perceptible external cause.

It was the use of unsuitable methods for the production of nitro-glycerine, and even more the constitution of the raw glycerine itself, which caused the many accidents in the nitro-glycerine factories. Before glycerine was produced by decomposition with steam under high pressure, and concentrated only by means of steam, glycerine of great purity and concentration was only obtained at high prices. In order, therefore, that the product should not be too expensive, the manufacturers of the nitro-glycerine used impure glycerine, which in addition to a large amount of water contained many foreign substances. Among the combinations which in addition to nitro glycerine result from the treatment of such a product with the nitration liquid are some of very low chemical stability and easily decomposed by slight outside influences, as, for instance, moderate increase of temperature. As this decomposition takes place suddenly either through heat or shock it is easily communicated to the nitro-glycerine, thereby causing an explosion, and in this we have a very simple solution of the many explosions which have frequently taken place in the isolated buildings, where prepared nitro-glycerine has been stored for a long period. Since improvements have been introduced in the manufacture of pure glycerine, its price has fallen so much that the nitro-glycerine works have at their disposal a substance of the greatest purity, and from this time reports as to explosions have become much rarer. By the use of a suitable process and glycerine of adequate purity, the manufacture of nitro-glycerine is no more dangerous than that of gunpowder, certainly less dangerous than that of fulminating mercury or of gun cotton. From the many works written on the manufacture of nitro products, particularly on the subject of gun cotton it seems pretty probable that the spontaneous decomposition of the preparations takes place especially where the nitric acid employed is not pure, but contains decomposition products of the nitric acid, and in particular nitrous acid. Therefore in the production of nitro-glycerine it is not sufficient to employ a very pure glycerine, but great care must be paid to the constitution of the nitric acid to be used, and for this reason manufacturers nowadays only use perfectly pure nitric acid, which before being employed is severely tested as to the absence of nitrous acid. As is well known, nitric acid easily decomposes when the temperature increases; as a result of the chemical reaction which takes place by bringing together a mixture of nitric acid and sulphuric acid with glycerine a considerable amount of heat is liberated, and thereupon it may happen that during the reaction decomposition products of nitric acid may be formed which in their turn react on the glycerine, resulting in the formation of easily disintegrated compounds. Therefore in the practical production of nitro-glycerine all the factors above mentioned must be most carefully taken into consideration, and in addition to the exclusive use of pure glycerine, and pure nitric acid, the temperature must be prevented from rising above a certain limit by means of a well-regulated system of cooling.

THE MANUFACTURE OF NITRO-GLYCERINE

The nitration acid—a mixture of about 5 parts of concentrated sulphuric acid, and 3 parts of nitric acid—is either obtained already mixed from the acid manufacturer, or else it is prepared on the spot itself. In the latter case great care should always be exercised, although the mixing of the two acids is quite a harmless operation. To this end covered pans fitted with an exhaust pipe for the evolved gases should be used, in which the stirring of the acid mixture is accomplished by compressed air. Splashing of the acids is thus avoided, and the mixing itself entails no danger.

As a rule the now ready nitration acid is lifted into a tall vessel, and for this purpose it is best to use compressed air. The acid reservoir must stand high enough so that in the natural descent of the liquid in the course of the manufacture, the acid mixture may flow to the nitration apparatus, the nitro-glycerine mixture to the separator, and the separated nitro-glycerine to the washhouse without being carried or even lifted. The "montejus," which are employed for the lifting of the acid mixture, consist either of lead lined, or polished wrought-iron, or cast-iron pans. Lead-lined vessels have not proved suitable, as it is unavoidable that in certain parts the lead should detach itself and then the exposed iron is all the more easily attacked by the acid. Cast-iron pans are very resistant to the action of acids, but they must be very strong in order to stand the great pressure which, on account of the high density of the nitration mixture (about 1·7), amounts to three atmospheres.

The nitration takes place in large leaden vessels which have been soldered with the hydrogen flame, with a diameter of about 1 metre, by 1 metre high; they are able to contain a weight of 100 kg of distilled glycerine at 31° Bé., 150 kg of sulphuric acid, containing 98 per cent mono-hydrate, and 250 kg of nitric acid of specific gravity 1·501, when a yield of about 212-215 kg. of nitro-glycerine will be obtained. In the apparatus there are about 100 m of cooling coils of 35 mm. diameter, which are used for cooling during nitration. Further, at the bottom of this vessel there are two pipes funnel-shaped at the end, and provided with small orifices. They are employed for the introduction of the compressed air, by means of which the mixture during nitration is vigorously stirred and kept in violent motion. The apparatus is closed with a cover fitted with a glass window, through which the progress of the reaction may be observed. The resulting fumes escape into the open by means of a vapour outlet. The bottom of the nitration apparatus is either inclined to one side or else flat and funnel-shaped; at the lowest point there is a very wide waste tap of clay. Underneath this there is a large water-tank containing water four times the capacity of the apparatus. If during nitration, in spite of continued stirring and cooling, the temperature in the apparatus should rise to 40°, then the workman should turn on the tap, which must be very wide, so that the apparatus is emptied in a short time, and the mixture may flow into the water-tank. Only in this manner can an imminent explosion be prevented In order that the nitro-glycerine mixture may flow to the separator, a funnel is placed under this tap, connecting it with the pipe leading to the separator. For observing the temperature, thermometers are fixed inside the apparatus, with a clear scale, the bulbs of which dip into the mixture. The nitration takes place at 28-30°, for cooling the mixture well water is generally used, and is allowed to flow through the cooling coils A quantity of about 100 kg. of glycerine is nitrated in about 30 minutes

Larger quantities of glycerine than 100 kg are seldom nitrated at one time; on the other hand, in America quantities of 2000 kg. at one time are treated in large, oval pans, in which there is an axletree with an eight-paddled wheel attached, which when rotating forces the glycerine in under the acid mixture. More certain and more suitable, however, is the employment of the Ballabene air-stirring process, which also allows the use of glycerine heated to 34°. At this temperature the liquid is much thinner and mixes more easily with the acid. Thereby local decomposition is avoided, which, moreover, is largely to be attributed to the great purity of the glycerine and the acid employed.

The glycerine flows out of a large number of fine holes pierced in a ring-shaped lead pipe, placed at a suitable height above the acid mixture, and in order to expedite the outflow of the glycerine, as a rule it is necessary to use compressed air on account of the thickness of the liquid.

The buildings in which the nitration takes place are constructed of light beams and boarding, and surrounded with a high wall of earth, on the one hand to deaden the violence of any possible explosion and on the other hand to give the workmen an opportunity, in case of threatened danger, to seek safety at once.

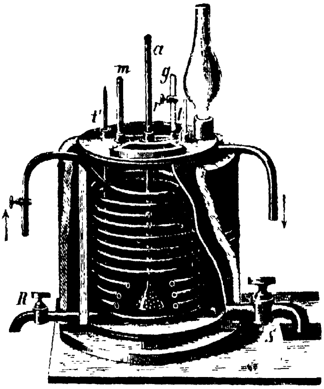

Fig. 3.

A nitration vessel of an older pattern is shown in Fig. 3. The glycerine flows through the pipe S which can be closed by means of the stop-cock R. The air-stirrer A is pierced at the bottom with holes like a sieve. The acid is then poured in through M; the thermometers T enable the temperature to be observed. The tap R serves for the purpose of emptying off the finished nitro-glycerine mixture; S is the safety tap which projects over the water-tank. For cooling purposes the cooling coil, which is plainly shown in the drawing, is used. In addition the nitration vessel is surrounded with a second jacket inside which cooling water is also circulated. As is already seen from the foregoing, two or more cooling coils are now used, and two or more compressed air-stirring devices in case one should suddenly fail. Moreover the waste-cock R can be dispensed with, and now only the safety-cock S is employed in the manner indicated.

A nitration apparatus of newer type, according to O. Guttmann, is arranged as follows: the acid mixture, generally 450 kg. of sulphuric acid and 250 kg. nitric acid per 100 kg. glycerine, is prepared in a large iron vessel. From here it passes through a cooling case into a storage receptacle or "montejus," and by means of compressed air it is then forced into the nitration vessel. These apparatus (Fig. 1), consist of a leaden vessel A, free from zinc, which stands in a wooden vat B and is fitted with a number of air-supply pipes C, cooling coils D, fume or vapour-discharge pipes F, thermometers E, and admission pipes for the acid G, and for the glycerine H. The cover can be removed, but during the operation is rendered airtight, by means of cement or linseed oil putty. In the pipe F there is a spy-glass inserted. The bottom of the apparatus is inclined to one side, and at the lowest extremity

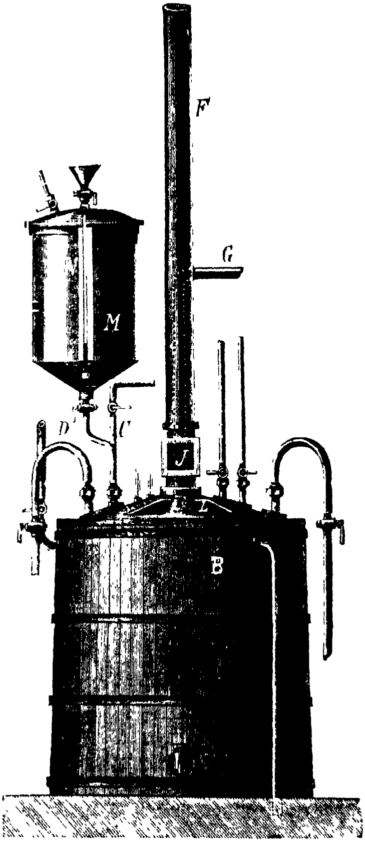

FIG. 4.—Nitration apparatus.

there is an outlet with a clay tap. The panes of glass L serve for the purpose of enabling the operations in the apparatus to be observed. It is placed over a pipe through which the whole contents can be quickly emptied into a large water-tank in case any danger of explosion should occur, or the temperature of the reacting mixture should rise considerably.

In order to avoid this, cooling should go on continually during the operation by means of water which flows through the cooling coils as well as through the space between the leaden vessel and the wooden vat. The glycerine is then poured drop by drop into the cooled acid mixture, when the temperature should not exceed 30. For the reception of the glycerine the wrought-iron cylinder M with the gauge N is used, into which compressed air is introduced through O. It forces the glycerine through the pipe H to the bottom of the nitration vessel. The resulting nitrous acid fumes escape through F, and the best plan is for them to be absorbed in a Lunge-Rohrmann tower.

When the nitration is accomplished, the nitro-glycerine mixture flows to the separator, where it is allowed to remain for some time for the purpose of separating the nitro-glycerine from the acid.

These separators are large, square, funnel-shaped, leaden vessels, on one side of which there is a glass window, and they are closed with a glass cover. From the lowest side of this separator there runs a leaden pipe fitted with a clay tap and a small pane of glass. On emptying, the waste acid first flows out; this passes through a funnel pipe into a conduit leading into the separating building. As soon as the first drops of nitro-glycerine can be seen through the observation glass, the separation can be carried out with great speed; the tap is turned off for a minute, and the funnel pipe moved to a tank partly filled with water, from which there is a pipe leading to the washhouse, and the tap is again turned on. In this tank the separated but still very acid nitro-glycerine is poured into a lot of water, when again compressed air is used for stirring. By this dispersion in water, any likely decomposition at this stage of the production is obviated. From here the raw nitro-glycerine dispersed in the water flows to the washhouse, where it is submitted to further purifying. This is accomplished by letting it flow into a leaden vat filled with cold water, stirred by air; after two or three changes of water and the use of hot water, it is finally thoroughly neutralized with soda and the now purified nitro-glycerine filtered. Great care must be taken in regard to the entire elimination of the acid, for glycerine which is not completely acid free may, though perhaps only after a time, decompose and explode.

For the separation of nitro-glycerine and waste acid, the separating apparatus shown in Fig. 5, p. 210, is used. It consists of a square, leaden vessel, with a conically shaped base, supported by a strong wooden frame or stand A. B and C are cross bars and sheets of lead which close it from the top. Gases can escape through the pipe D, which is fitted with an observation glass E. Through the cover a thermometer is fixed which dips into the liquid, and there is also a pipe K which admits the mixture coming from the nitration apparatus. The pipe at the lowest extremity is fitted with a spy-hole F and continues in pipe G and is fitted with two or three taps H.

When the nitration mixture is admitted, it remains standing for about half an hour, whereupon the nitro-glycerine flows through J to L in such a manner that only a little nitro-glycerine is floating on the waste acid. This is separated from the acid by means of the taps G and H. The nitro-glycerine is then washed in L and stirred with compressed air, introduced through N, and the washing water then flows away through M.

The waste acids which have been separated from the nitro-glycerine are passed into the separator for the purpose of further extraction, where they are allowed to remain undisturbed for a few days, in order that any residue of nitro-glycerine should rise to the surface, and be collected. In order to extract the nitric acid a denitrificator is employed, a four metre high cylinder with acid-proof stone lining in which the acid flows over pumice stone or coke, whilst from underneath air and water vapour are introduced. By this means the acid splits up into nitric acid of about 26 Bé., and sulphuric acid of 56 Bé. which can be sold as waste products.

CHAPTER VII

PROPERTIES OF NITRO-GLYCERINE

THE theoretical yield of nitro-glycerine would amount to 246·7 parts from 100 parts of glycerine; in reality, however, only 210-215 parts are obtained according to the method of working. It was endeavoured, therefore, to increase this yield, and several methods have been resorted to. Thus, according to the English patent 2776 of February 10, 1905, it is recommended to use the waste acids instead of the freshly prepared nitrating acids, only adding sufficient fresh acids to restore them to the original composition; thereby the yield is said to be increased up to 228 parts. According to the English patent 1658 of March 19, 1906, Nathan and Rintoul, on the contrary, recommend as much as possible the use of water free acids. They nitrate with a mixture composed of 2·8 parts of nitric acid and 3·4 parts of fuming sulphuric acid, when a yield of 230 parts of nitro-glycerine results. According to Stutzer, 100 parts of glycerine nitrated with a mixture composed of 267 parts of sulphuric anhydride, and 264 parts of nitric acid yield 222 parts of nitro-glycerine, which is decidedly more than is obtained with the older method.

The separation of nitro-glycerine from waste acid is often delayed by the separation of gelatinous silicates. It has been attempted to prevent the appearance of this phenomenon by addition of various substances, such as paraffin, or fatty acids of high molecular weight (0.5 to 2 parts per 1000 of glycerine by weight) or by the addition of 0.002 per cent sodium fluoride. The sodium fluoride acts in such a manner that silicic acid is converted into silicofluoride.

Glycerine has three hydroxyl groups, so that it can form three nitrates, that is three nitric acid esters, according as all three or only two, or only one hydrogen atom is replaced by the NO_2 group. As ordinary nitro-glycerine, that is tri-nitro-glycerine, freezes easily and in its frozen condition is fairly susceptible to a blow, while on the other hand, other glycerine nitrates do not possess this characteristic, and also in a liquid condition are less sensitive, they have been more in favour lately. Di-nitrate, for instance, as long as it is free from water, does not become solid, even at the lowest winter temperatures, but it absorbs water from the air, and then also freezes fairly easily.

Less sensitive and easier to produce is tetra-nitro-glycerine

$$\begin{array}{l} C_3H_5(O.NO_2)_2 \\ C_3H_5(O.NO_2)_2 \end{array} O$$

which is produced by nitration of di-glycerine.

Di-glycerine is produced by polymerization of two molecules of glycerine and the splitting off of one molecule of water. It is sufficient that to the glycerine to be nitrated 20-25 per cent di-glycerine be added, in order to obtain nitro-glycerine which will be sufficiently resistant to cold.

By the nitration of chlorhydrin (see p. 14), di-nitro-mono-chlorhydrin, $C_3H_5Cl(ONO_2)_2$, which is not hygroscopic, can be obtained, and even at temperatures of −30° it will not freeze. It is easily dissolved in tri-nitro-glycerine, and an addition of 20 per cent is sufficient to render the nitro-glycerine non-freezing under not too extreme circumstances (D.R.P. 183,400). As di-nitro-mono-chlorhydrin is, moreover, much less sensitive than nitro-glycerine, its use is more practical. Nitrated chlorhydrin can be dispatched in quantities up to 200 kg. by the German railways, whereas the transport of nitro-glycerine is altogether prohibited.

Pure nitro-glycerine that is entirely free from acid and water, is a colourless or at least a very faint yellow liquid, with a sweetish burning taste, and odourless. The specific gravity of pure nitro-glycerine is 1.6.

Nitro-glycerine is practically insoluble in water. With ether and methyl alcohol it is miscible in all proportions. Before the use of nitro-glycerine for dynamite in its non-dangerous state had been discovered the explosive oil was dissolved in methyl alcohol. In this solution the substance was deprived of its explosive qualities. By adding water it was separated again from the methyl alcohol solution, with its usual explosive qualities.

In cold alcohol nitro-glycerine dissolves but little; on the other hand it dissolves well in this solvent at 50° C. It easily volatilizes above 100° without decomposition. In a pure state it does not easily decompose.

At 15° it thickens without congealing. Subjected for a time to a temperature of 2° it crystallizes. Even a temperature of 8° C., if it acts long enough on the nitro-glycerine, can convert it into the crystalline state. It may be said that nitro-glycerine at temperatures of 8° to 11° C. passes from the liquid to the solid state, but in this respect various nitro-glycerines differ. Some nitro-glycerines at a temperature of 12° C. require ten to fourteen days before congealing, whereas others require more or less time.

If nitro-glycerine is submitted for some time to a temperature of practically 100° C., it shows great resistance to congealing. Very minute particles or quantities of impurities suffice to delay or hinder crystallization. If nitro-glycerine is quickly congealed it crystallizes to a whitish yellow opaque mass.

The frozen explosive oil thaws again at about 11°. For a long time it was presumed that on freezing, explosive oil expanded about $\frac{1}{11}$th, whereas Mowbray, in the case of the nitro-glycerine produced according to his method, ascertained a contraction of $\frac{1}{12}$th of the original volume. Recently, however, the density of the Nobel liquid and solid nitro-glycerine has been found to be 1·599 and 1·735 respectively, which shows a contraction of [illegible]. This last fraction corresponds entirely with that obtained by Mowbray, and therefore the physical constitution of the Nobel explosive oil is identical with that of Mowbray.

Explosive oil even in small quantities is poisonous. In this connexion Schuchardt has experimented on himself, and reports as follows. He swallowed a drop of nitro-glycerine and soon experienced giddiness and weakening of the sight, headache, lassitude, sleepiness and a strong, spicy taste and burning in his throat. An hour later, when by inadvertence he swallowed more nitro-glycerine, he soon noticed an increase in the symptoms. Then followed unconsciousness, giddiness, trembling, violent throbbing, headache, and aversion to light; a feeling of cold was followed by a feeling of heat, nausea without vomiting ensued, but there were no cramps, and the following day no further effects of the nitro-glycerine were noticeable.

Workmen who use nitro-glycerine for blasting purposes easily get headaches. This has been explained by the fact that nitro-glycerine easily penetrates the skin, and so passes into the blood. In order to avoid direct contact of the skin with nitro-glycerine the workmen are allowed to wear rubber gloves, particularly in the preparation of dynamite, but most of them find that these gloves hinder them in their work, and do not use them.

As antidote to such nitro-glycerine poisoning, black coffee has been recommended, rubbing in of washing soda lye, and aqueous solution of hydriodic acid, which is said to decompose nitro-glycerine and reforms the glycerine.

In order to detect the presence of the minutest particles of nitro-glycerine, it should be mixed with aniline and concentrated sulphuric acid, when if traces of nitro-glycerine are present a purple colour ensues which turns green on diluting with water.

Explosion of Nitro-Glycerine and the Resulting Gases

Nitro-glycerine explodes when heated to 280° or by some violent shock, or, finally, by violent and sudden pressure brought about by the explosion of the strong fulminating preparations (fulminate of mercury) with which it finds itself in contact (Nobel's fuse cartridges). In each of the three cases it is heat alone, or work converted into heat, which brings about the explosion. If nitro-glycerine is carefully warmed, then at about 100° decomposition sets in with liberation of hyponitrous acid. It is stated that nitro-glycerine can be volatilized entirely, when gradually heated, without any explosion taking place.

On heating, nitro-glycerine behaves as follows: at 185° it boils with evolution of yellow fumes, at 194° slow volatilization takes place, at 200° rapid volatilization, at 218° strong combustion, at 241° (slight) detonation, at 257° strong detonation, at 287° weak detonation, with flame. At red heat the nitro-glycerine volatilizes without detonation, because it passes into the so-called spheroid condition.

A very important characteristic of nitro-glycerine is that the temperature at which it explodes does not coincide with its ignition temperature, but is much higher. Therefore nitro-glycerine (in contrast to gunpowder and flocculent gun cotton) belongs to the *indirect explosive substances*. This quality is of the highest practical importance, and it is thanks to this quality that explosive oil at ordinary temperatures when ignited burns with difficulty but never explodes. It has burnt out before it has reached explosion point. Therefore there is scarcely any danger when nitro-glycerine ignites, provided that not too great quantities of explosive oil are attacked by fire.

In the case of direct ignition nitro-glycerine as already stated does not explode. During some experiments which Nobel conducted in the presence of several scientists at Stora Ahlby in Sweden in 1865 nitro-glycerine could not be ignited by touching the surface with a red-hot iron bar; ignited with a chip of burning wood it burned with flame but without explosion, and the flame died out immediately the wood was removed. If explosive oil is submitted to gradually increased, and finally very strong pressure, apparently it does not explode. On the other hand it explodes each time in the case of sudden strong pressure, for instance a heavy blow. But the explosion of the portion subjected to the pressure does not communicate itself to the remainder of the mass.

When at Rennkoppel near Hamburg in March, 1866, Nobel shook some drops of nitro-glycerine on an anvil and had it violently hammered, only the nitro-glycerine that came in direct contact exploded with a loud report, but the explosion did not extend. A small bottle containing nitro-glycerine can be thrown against a stone in such a manner as to break, but the preparation will not explode.

Formerly there existed the erroneous opinion that frozen nitro-glycerine was more susceptible to blow or shock than the liquid nitro-glycerine. The fact is, however, as exhaustive experiments have proved, quite the contrary. Simple reflection proves that according to physical laws this must be so.

The blow or pressure to which nitro-glycerine has been submitted is converted into heat, just as any checked motion or movement is converted into heat (compare, for instance, the heating of a wheel, when the brake is applied to a train). The blow or pressure administered to the nitro-glycerine must therefore be sufficiently powerful to raise the heat of the nitro-glycerine up to 180 (its explosion temperature). In order, however, to heat frozen explosive oil to 180 it is evident that more heat is necessary than would be required in the case of a similar weight of liquid nitro-glycerine to bring it to the same temperature. For as regards frozen nitro-glycerine heating for melting purposes must be applied, in a word the frozen nitro-glycerine must first of all be supplied with its latent heat of fusion. In this connection all practical experiments tally

Quantities of fulminating mercury, which certainly cause explosion of liquid nitro-glycerine, leave crystallized nitro-glycerine unaltered. Moreover, solid and liquid nitro-glycerine were placed in a thin layer on a flat anvil of Bessemer steel and a wrought-iron hammer was allowed to fall on the anvil. In this instance the average drop for detonation of the liquid nitro-glycerine was 0.78 m., whereas frozen nitro-glycerine only exploded at a drop of 2.13 m.

In any case frozen explosive oil should never be touched with sharp and pointed instruments, and should always be thawed in dynamite-heating or similar apparatus by the use of hot, not boiling water. If nitro-glycerine is not absolutely pure, very often, as in the case of impure gun cotton, spontaneous decomposition takes place, which may easily cause explosion. Then glyceric acid and oxalic acid are formed (by oxidation). At the same time the nitro-glycerine in process of decomposition turns green, and forms nitrous acid, nitric oxide, and carbonic acid. As nitro-glycerine is generally kept in well-closed bottles, the gases resulting from this spontaneous decomposition cannot escape, and therefore exercise great pressure on the nitro-glycerine. Under these circumstances the slightest blow or shock is sufficient to cause explosion.

As to whether such a decomposition is in progress may be known by the reddening of blue litmus paper dipped into the nitro-glycerine.

If explosive oil should explode in a closed room, it exercises very violent pressure. This is to be attributed to the considerable quantity of explosion gases which develop, as well as to the high combustion temperature caused by the explosion, when the gases expand to about eight times their original volume.

According to the experiments of Sarrau and Vieille, nitro-glycerine during explosion decomposes in the following manner:

$$2C_3H_5(O \cdot NO_2)_3 = 6CO_2 + 6N + 5H_2O + O$$

1 grm. nitro-glycerine liberates therefore

295 c.c. carbon dioxide
117 c.c. nitrogen
25 c.c. oxygen

at 0° and 760 mm. barometric pressure, consequently there results 467 c.c. permanent gases. The gas pressure amounts to 10,000 atmospheres.

In order to lower the sensibility, and at the same time to avoid the disadvantages connected with the use of liquid explosive substances, it is generally used in the form of Guhr dynamite or explosive gelatine.

In the former case the action is less than that of the corresponding weight of pure nitro-glycerine, in so far as the non-gaseous mineral substance absorbs a part of the liberated heat given off during the explosion. A further lowering of the explosion temperature is obtained by mixing with the dynamite salts containing water of crystallization, such as soda crystals or Glauber's salts. Such preparations offer relative security against the communication of fire to fire-damp or coal dust, and are used in mines under the name of Wetter dynamite.

In the second case by the production of explosive gelatines, the duration of the time of gasification is extended, which at the same time results in heat losses; whether this loss is counterbalanced by the fact that the nitro-cellulose completely burns the nitro-glycerine at the expense of the surplus oxygen must for the time being remain in abeyance.

In the technics of explosives nitro-glycerine has been applied in several ways; the first explosive preparation used by Nobel was constructed in such a manner that cartridge cases of sheet zinc, the diameter of which was somewhat smaller than that of the bore hole, were filled with gunpowder and so much nitro-glycerine was poured on it as would find room between the grains of powder. When the cartridges had been sunk into the bore hole they were covered with a layer of powder 22 mm. high. The charge was ignited by means of a quick match or percussion cap.

CHAPTER VIII.

DYNAMITE.

THE manifold drawbacks connected with the use of nitro-glycerine in the liquid state, and particularly also the endeavour to render the manipulation of the explosive oil less fraught with danger by mixing it with a non-active solid component, have resulted in the explosive oil being absorbed by porous, solid substances, and being employed in this new form under the name of dynamite.

Formerly under the designation dynamite only that preparation was understood that was obtained by the absorption of explosive oil by kieselguhr (kieselguhr dynamite No. 1).

At present dynamite applies to any explosive substance impregnated with nitro-glycerine, the nature of the absorption substance being immaterial.

Kieselguhr is erroneously designated infusorial earth, as formerly the diatoms of which it consists were considered to be infusorial plates, whereas they spring from a genus of plant to which algae belong. They are surrounded with a very strong silicic acid coating, and under the microscope the form is that of a dish, a boat, or a pipe. The appearance of kieselguhr is like that of flour and it is also similar to the touch; in a pure state the colour is white, generally, however, owing to different impurities, it is either yellowish, reddish, or greenish. Before being used for the production of dynamite the kieselguhr is roasted in order to destroy any organic matter that may cling to it, and it is then crushed. The best kieselguhr comes from the province of Hanover

The fairly extensive class of dynamites may be divided into two distinct groups, namely, dynamite with chemically non-active absorbing material, and that with chemically-active absorbing material. To the former really only kieselguhr dynamite No. 1 belongs. The silica which contains the absorbed explosive oil has no chemical action on the nitro-glycerine or its explosion gases, in the case of an explosion of dynamite No. 1, but remains on the contrary an entirely unaltered product of the explosion.

It is quite a different matter in the case of dynamite with a chemically active absorbent. The latter under all circumstances with its chemical components participates in the explosion, and by its co-operation alters the composition and active power of the explosive gases of the nitro-glycerine.

Dynamite with chemically active absorbent often has the effect of retarding the too rapid explosion of explosive oil, or dynamite No. 1, and of converting the violent blasting action of the explosive gases of the nitro-glycerine into a more driving or pushing action At the same time many of the kinds of dynamite are less dangerous to handle than dynamite No. 1, because they contain far less explosive oil than the latter. But owing to the fact, however, that the chemically active absorbent causes complete combustion of the dynamite, it results that many of these dynamites with a similar amount of nitro-glycerine in the cartridge are more efficient than dynamite No. 1.

Dynamites with chemically active absorbent can again be divided into three classes, and can be designated as follows:—

1 Dynamite, containing as ingredients kieselguhr dynamite (containing nitro-glycerine) and a kind of gunpowder mixture To this class belong *Lithofrakteur* which may be conveniently said to be composed of dynamite and barium nitrate-gunpowder, further *Kolonial* powder, a dynamite which is now no longer in use, which consisted of nitro-glycerine absorbed by a kind of explosive powder mixture, and finally *Brain's explosive powder*—a sulphur free powder-like mixture containing absorbed nitro-glycerine.

2. Dynamite, the absorbent of which is wood substance, or nitrated wood substance. To this class belong *Lignose* (wood fibre impregnated with nitro-glycerine), *Dualin* (nitrated saw-dust impregnated with nitro-glycerine), *cellulose dynamite* (a specially prepared wood material steeped in nitro-glycerine), as also *dynamites 2, 3, and 4* (a mixture of boring dust and saltpetre or similar substances, impregnated with nitro-glycerine).

3. Dynamite, containing gun-cotton, collodion cotton, and nitro-glycerine. Here we have *gun-cotton dynamite* and *explosive gelatine* (gelatine dynamite).

Of all these different dynamites the most important are only: Kieselguhr dynamite 1, dynamites 2, 3 and 4, cellulose dynamite, explosive gelatine, and lithofrakteur.

(*a*) DYNAMITE WITH CHEMICALLY NON-ACTIVE ABSORBENT.

Kieselguhr Dynamite.—It is said that chance led Nobel to the very important discovery of this dynamite. For some time infusorial earth had been used for packing the tin cans containing the explosive oil; one of these ran over, and the properties of the infusorial earth were observed, and experiments confirmed that the explosive action of the nitro-glycerine was entirely preserved, but on the other hand the explosive properties considerably diminished

According to other statements, however, the discovery of dynamite is to be attributed to the mine inspector Schell at Grund near Klaustal, in the Hartz, who first used nitro-glycerine mixed with a light porous earth, which absorbed it. However this may be, Nobel in any case first introduced it into technical blasting.

MANUFACTURE OF KIESELGUHR DYNAMITE.

The infusorial earth used as absorbent for nitro-glycerine is found in many places, but that occurring in an extensive layer near Oberohe (province of Hanover) is particularly fine and suitable for the manufacture of dynamite

The drawbacks of infusorial earth for the manufacture of dynamite are the moisture contained, organic matter, and coarse grains. In order to remove the two first the infusorial earth is heated to redness. It is placed in a furnace or stove containing four super-imposed trays, in which the infusorial earth is gradually shifted from the upper to the lower. In order to remove the coarse grains the heated infusorial earth is crushed by hand rollers, and shaken through a sieve which retains any remaining coarse grains.

The mixing of the nitro-glycerine usually takes place in the same shed in which the plant employed for the final deacidifying of the nitro-glycerine is housed. One hundred and fifty kg. of explosive oil is poured over 50 kg. of infusorial earth contained in flat wooden cases, and the workmen knead this mass with their naked hands. As nitro-glycerine easily penetrates into the skin, the workmen were given rubber gloves to protect them against the poisonous effects of the nitro-glycerine. They, however, soon dispensed with the gloves, finding it easier to work with their bare hands. In half an hour's time the mixture is ready. The mass is then placed on an iron wire sieve, the meshes of which are about 1 mm., and pressed through the holes of the sieve by hand. This is now kieselguhr dynamite which only needs to be placed in cartridges.

The dynamite cartridges are small cylinders containing pressed dynamite enclosed in strong parchment paper Three kinds of dynamite cartridges exist, (1) ordinary dynamite cartridges of 3-10 cm. long and 3 cm. diameter; (2) fuse cartridges, 3 cm. long and 3 cm. diameter; (3) fuse cartridges for frozen dynamite.

The first-named cartridges generally have their paper covering removed and are forced into the borehole. The fuse cartridges serve for the reception of the percussion cap, that is the quick match which is contained in the percussion cap. The cartridges of frozen dynamite, in addition to ordinary dynamite, contain a mixture of saltpetre and rosin or of potassium chlorate and antimony sulphide or similar ingredients, which are first ignited by the percussion cap, and these cause the frozen dynamite to explode.

The moulding of the cartridges is accomplished as follows; about 5 kg. of dynamite are placed in a linen receptacle open at the bottom and there connected with a funnel-shaped brass device. A piston reaches into this, the upper part of which penetrates the linen sack and can be moved up and down by means of a lever. At the highest position of the piston the orifice of the funnel remains open, so that the dynamite can enter, and then when the piston is lowered into the funnel, and the pipe steel piece connected therewith is pressed down, it comes out underneath in the form of a solid cylinder The upper edge or border of the linen sack is connected with the lever of the piston, which therefore shakes it up and down. Moreover, wooden valves are fixed to the sides of the linen sack which are also connected with the lever, and shake the bag to and fro So the dynamite is moved along continuously as the piston is worked up and down.

The pipe screwed to the bottom of the funnel is of the same diameter as the dynamite cartridges. When by the movement of the piston lever this pipe is quite filled, the corresponding sheet of parchment is rolled round and the parchment cylinder placed under the mouth of the pipe. A further movement of the piston lever brings along the dynamite cylinder which takes the parchment case.

As a rule a dynamite factory has ten smaller cartridge sheds in each of which two machines and two men are working. Each cartridge shed is separated from the other by a wall of earth of 4 metres. Often there is a complete reserve factory built, in case those working are partly or entirely blown up. The sheds are lightly built of wood and the roof and side walls lined with straw, so that in winter the temperature can easily be maintained at 15°. The light comes in from outside, and the floor is of loose fine sand.

The danger connected with the manufacture of dynamite is the mixing of the infusorial earth with the explosive oil, as well as the forcing of the prepared dynamite into the cartridge moulds. Unfortunately accidents are not an exception in connection with this operation. It may, however, confidently be said that the greater number of the explosions would not have occurred had the necessary care been exercised. It is just the relatively great lack of danger with which dynamite may be handled that only too easily inspires the ignorant workmen with a feeling of security Only too frequently dynamite is handled with the utmost carelessness, or rather mishandled, and it is really wonderful that explosions are not more numerous. Only the most careful enlightenment as to the explosive characteristics of dynamite, the most accurate instructions as to its manipulation, and absolute severity in case of any infringement will in future help to prevent these explosions

The Properties of Dynamite

Dynamite is a dough-like, plastic mass of 1·4 specific gravity of a yellow reddish colour, and greasy to the feel, and odourless. It consists of about 75 parts of nitro-glycerine and 25 parts kieselguhr.

Dynamite can only be made to explode by means of explosive substances, percussion caps, red-hot metals, sudden heating to a high degree, or by a violent blow or shock. Coming into contact with light, a match or burning fuse, it burns without exploding just like damp paper. The reason for this is that dynamite in common with all nitro-glycerine preparations belongs to the indirect explosive substances, because its explosion temperature is considerably higher than its ignition temperature.

The kieselguhr of the dynamite retains the absorbed nitro-glycerine so tenaciously that even strong pressure will not force it out. The reason why such a considerable addition of kieselguhr to the nitro-glycerine should diminish the explosive action to such a slight degree is that this admixture does not disturb the uninterrupted cohesion of the explosive substance. The detonating fulminating mercury in the percussion caps, surrounded by such a mixture, is at all points in contact with a portion of the nitro-glycerine without the cohesion of this latter substance being disturbed. Therefore, the detonation spreads through the mixture with as much ease as if the liquid were not mixed with such a substance. If, however, a solid, inert body is mixed with a similar solid, finely distributed, explosive substance, then the development of the explosion, or its rapid transmission is checked, owing either to reduction in the contact between the detonator and the substance, the explosion of which should be effected by the former, or to the resistance offered by the intervening non-explosive particles to the rapid spreading of the explosion, or to both causes. Thus, for example, the easy explosion of fulminating mercury is considerably weakened if mixed with a non-active, fine powder such as Spanish white.

Brought in contact with fire or glowing bodies, dynamite even in quantities of several kilograms burns without exploding if it is not packed into too tight casings. Temperatures under 60° C. even of prolonged duration have no detrimental effect on dynamite. It can, therefore, be exposed to the heat of the sun without risk of injury.

On coming into contact with the mucous membrane of the nose or the mouth dynamite can cause very violent headache; precautions should therefore be taken against such direct contact which is all the more easy as the dynamite is supplied packed up in cartridges.

Through violent concussion between hard bodies, dynamite will explode; on the other hand even violent blows of wood against any substratum will not cause it to explode. If dynamite is placed on an anvil only the most powerful hammer blows will cause the explosion of the parts directly in contact with it. In general, therefore, dynamite is a harmless substance to manipulate. However, its slightly dormant, highly explosive power should constantly be borne in mind, and the greatest care should always be exercised when handling it.

A well-known peculiarity of dynamite is that preferably it only exercises its tremendous power on the nearest surroundings, namely, a solid substratum. An example of this is given at the Rammelsberger Mining Works in connection with the advantageous breaking up of the blocks of iron pyrites resulting from the blasting operations. A dynamite cartridge is placed upon the upper surface of such a block of ore, thickly covered with damp clay, and then ignited. The downward pressing force of the exploding dynamite shatters the mass, or loosens its cohesion in such a manner that it is easily broken, or completely blasted by a second charge of dynamite.

At temperatures under 8 the nitro-glycerine in the dynamite freezes, and the latter congeals or hardens. Frozen dynamite is thawed in the same way as frozen nitro-glycerine and the same precautionary measures must be taken

Frozen (that is entirely, not partly, frozen) dynamite is less sensitive to blow, shock, shot, and heat than non-frozen dynamite. The reasons for this are of course the same as in the case of frozen nitro-glycerine.

The relative lack of danger connected with the manipulation and transport of dynamite has been proved by several experiments. Of these we only mention the better known Swiss experiments of Bolley, Pestalozzi and Kundt. These experiments were also undertaken with a view to determining the force of the shock necessary to cause ignition. To this end metal cartridges in which the explosive substance was closely packed were shot out of an air-gun against a horizontal wall 13½ m. distant. The thinly incased cartridges exploded, those with thick cases did not, very likely owing to their lesser initial velocity. This was ascertained at 40 m. per second. With a Bickford fuse not even ignition was obtained.

APPLICATIONS OF KIESELGUHR DYNAMITE.

The advantages of dynamite as an explosive over black powder consist in the far simpler and more rapid manufacture of dynamite, in the economy effected in time, money, and labour, and in the greater availability of dynamite, for example in blasting damp rock or without the necessity for tamping.

For blasting operations under water, waterproof casings for the dynamite cartridges are necessary.

No other explosive has attained anything like such a wide application as dynamite in its different grades (dynamite 1, 2, 3, and 4). In civil practice it is used for the blasting of stone, wood, ice, iron, masonry, for loosening the soil in agriculture and horticulture, as well as for the removal of stumps of trees in forestry.

In warfare it is employed for the destruction of cannon, masonry, palisades, as well as for submarine blasting, as filling for sea mines and torpedoes, in so far, in the latter case, as compressed gun cotton is not used.

The violent shock produced by the explosion under water stuns the fish for some distance round, and they collect on the surface of the water.

This was taken advantage of during the siege of Paris to carry out fishing on a large scale. Also poachers more often than not make use of this very convenient method of illegal fishing.

Kieselguhr dynamite No. 1 is up to the present about the only representative of dynamite with chemically non-active absorbent.

Prepared calcined clay has also been recommended as a substitute for infusorial earth. English china clay, at present being exported in large quantities to the Continent (to paper and stoneware factories), is particularly suitable for this purpose. If this clay, similar to kaolin, is gently heated and then finely ground, it is by no means inferior to infusorial earth as an absorbent, in fact it is even superior on account of its alkaline properties. This small amount of alkali would at once bind the acid resulting from the decomposition of the nitro-glycerine, that is it would render the decomposition harmless. Moreover, by the application of heated clay in many cases the often very distant transport of infusorial earth would be avoided. In order, however, to distinguish this kind of dynamite from the ordinary kieselguhr dynamite it should be called "clay dynamite". Boghead coal ash has also been recommended as an absorbent.

(*b*) DYNAMITE WITH CHEMICALLY ACTING ABSORBENT.

Here we have, as has already been mentioned, lithofrakteur (Kolonial powder), Brain's explosive powder, lignose, dualin, cellulose dynamite, dynamites Nos. 2, 3 and 4, gun-cotton dynamite and gelatine dynamite (explosive gelatine). We will discuss these explosives in their order:—

1. *Lithofrakteur.*—Very incomplete and often erroneous statements have been made with regard to this explosive substance discovered by Krebs Bros. & Co. and manufactured in Cologne, and which

in its action is practically similar to kieselguhr dynamite.

Krebs' lithofrakteur contains in 100 parts 55 parts of nitro-glycerine, and although this is 20 parts less than in kieselguhr dynamite, yet, in spite of this, the explosive power of lithofrakteur is greater than of dynamite No 1 on account of the entire burning of the nitro-glycerine and the presence of other mutually reacting chemical substances, which in an explosion develop a very high temperature and a large quantity of highly expanding gases. Owing to the nature of these substances and the complete burning of the nitro-glycerine in the lithofrakteur, these gases consist only of carbonic acid, hydrogen, water gas, and a trace of sulphurous acid; they are free from steam-vapour and in no way injurious to health, neither do they dim the light of the lamps in the mines.

The 45 parts other than nitro-glycerine which compose lithofrakteur contain only 21 parts of infusorial earth and 24 parts of other absorbing substances which not only keep the nitro-glycerine in suspension, but in the case of an explosion are almost entirely converted into gases of high temperature and dilation.

These substances are carbon, prepared bran, prepared sawdust, barium nitrate, sodium sesqui-carbonate, manganese, and sulphur. They are chosen in such proportion that in an explosion they develop the highest temperature and largest quantity of gas, and the following points of view are considered: Charcoal, prepared bran and prepared sawdust, free from resin and mixed with saltpetre, are not only good absorbents for nitro-glycerine, but in an explosion they are completely transformed into carbonic acid and water vapour owing to the surplus oxygen.

The small addition of sulphur is also converted into gas, sulphurous acid, whereas the barium nitrate and manganese at a high temperature give off a large quantity of free oxygen which effects the entire combustion of nitro-glycerine, carbon, bran, sawdust and sulphur, and causes the highest possible temperature.

Finally, the addition of a small quantity of sodium sesqui-carbonate has a twofold object. In the storing and manufacture of lithofrakteur this acts as a protection against spontaneous combustion, which would be possible in the case of nitro-glycerine, which through carelessness might not be quite free from acid, because such traces of acid would be neutralized by the presence of the sodium sesqui-carbonate. Further, if lithofrakteur is ignited, the sodium sesqui-carbonate is decomposed into free carbonic acid and caustic soda owing to the great heat resulting from the explosion, whereby the quantity of dilating gases and power of the explosive substance are considerably increased.

On setting fire to a lithofrakteur cartridge in the open air, not the slightest trace of smoke is to be observed, neither is any odour perceptible. Lithofrakteur burns evenly with an orange-yellow flame and leaves a gritty, grey ash.

This ash treated with water and filtered shows only a weak barium reaction, a proof that the barium nitrate (soluble in water) contained in the lithofrakteur has been completely decomposed on burning, barium silicate being formed, and the nitrogen of the nitric acid in the original barium nitrate has been liberated and has exercised its expansive power.

Moreover, there is no sulphur compound to be found in the filtrate. On treating the residue with hydrochloric acid there is no development of carbonic acid; a very faint reaction for sulphuretted hydrogen is perceptible The small amount of sulphur has also been dissipated

The remaining organic substances have, on burning, partly hastened this decomposition, and owing to the formation of their own gases have advantageously increased the explosive power of the explosive substance

If the composition of lithofrakteur is more carefully examined, it will be found to contain practically the same substances as in black powder, mixed with dynamite. Instead of the potassium nitrate in the powder, barium nitrate is in this case substituted. The remaining substances supply the carbon, while nitro-glycerine and infusorial earth (ingredients of kieselguhr dynamite) make up the other part of the explosive.

Lithofrakteur can, therefore, be considered as a connecting link between powder and dynamite, and it is so indeed. On the one hand it possesses in an explosion the driving force of gunpowder, and on the other hand the shattering force of dynamite, and for these reasons it is in all cases preferable to the other two when a more heaving and shattering than crushing action is desired in rock blasting. The development of gases during the burning of lithofrakteur is slow, and acts without any loss of power through some distance on the resistance offered it.

Lithofrakteur is highly insensitive to strong pressure and shock. A bullet shot through a lithofrakteur cartridge does not cause ignition. A bombshell charged with 330 g. was fired off and on striking did not burst. A tin containing 2·5 kg. of lithofrakteur was shattered on falling from a height of 50 m., but did not explode however. On the other hand lithofrakteur exploded by a heavy blow of iron on iron.

According to Luckow, the best quality of lithofrakteur should have a capacity of six or seven times the amount of gunpowder. Experiments which were carried out with dynamite and lithofrakteur showed the following results:—

A cartridge charged with 20 g. of lithofrakteur and ignited indicated on the Brisanz meter 12·25°, and a cartridge charged with 20 g. dynamite 14·50°. Another cartridge with 20 g. dynamite (with 75 per cent nitro-glycerine) indicated 14·50°, on the other hand a cartridge of lithofrakteur of 27·25 g., that is with the same nitro-glycerine contents, indicated 15° on the Brisanz meter.

The greater action in the case of lithofrakteur with the same amount of nitro-glycerine in the cartridges, must therefore be attributed to the other added substances, whereby evidently lithofrakteur is distinguished from dynamite.

More often than not it has been observed that dynamite cartridges, particularly when they are long, only explode partly so that the lower part which is further from the percussion cap remains unburnt; or in blasting operations without a bore hole with loose tamping, part of the cartridge is hurled away without exploding and is, therefore, without effect. This has not been found to occur in the case of lithofrakteur owing to the easily inflammable substances dispersed throughout the whole mass, and its not too rapid combustion.

A further advantage of lithofrakteur over dynamite is that in damp and rainy weather, when explosive material must be used without casing, it can always be made explode whereas in a similar case dynamite sometimes fails.

Another composition of lithofrakteur is given as follows:-

54·5 parts nitro-glycerine, 14·75 parts barium nitrate, 2 parts manganese, 2 parts soda, 2 parts boring dust, 1 part bran, 7 parts sulphur, and 16·75 parts kieselguhr.

2. *Kolonial Powder.*—In the same way as lithofrakteur may be considered as a kieselguhr dynamite mixed with ingredients of gunpowder, so kolonial powder is a somewhat modified form of black powder mixture impregnated with nitro-glycerine.

Kolonial powder was introduced into commercial use by Wasserfuhr, of Cologne. Freshly manufactured, it gave splendid results. After experiments at Bonn the preparation, under favourable circumstances, was said to have an action five to six times as strong as ordinary powder. On being put by for some time it was found that the nitro-glycerine separated and thereby its use was attended with danger. For this reason it has not been manufactured for many years now.

3. *Brain's Explosive Powder.*—This powder is the invention of the English mining engineer, W. B. Brain, and consists of 60 per cent of a composition consisting of potassium chlorate, potassium nitrate, charcoal, and oak sawdust and 40 per cent of the same explosive oil.

The force of this explosive may be taken as 25-30 per cent greater than that of a similar weight of dynamite. It is characteristic of this explosive that its action increases in proportion as the resistance and hardness of the material to be blasted increase. In the basalt quarries its action is a tremendous one, as experiments in the Adrian basalt quarry near Oberkassel in the Siebengebirge have proved. On the other hand its action in Loess is very slight as the mass is too loose and soft. Ignited with a quick match but without a percussion cap, the powder burns quickly with a red fairly smoky flame but without exploding.

4. *Lignose.*—Whereas the three kinds of dynamite which we have been discussing may well be considered as mixtures of nitro-glycerine with chemic-

ally acting absorbent, that is dynamite with somewhat modified components of black powder, the following kinds of dynamite are mixtures of wood substance, that is nitrated wood substance with nitro-glycerine to which sometimes an oxygen carrier, e.g saltpetre, is added. Lignose is wood fibre impregnated with nitro-glycerine. It was invented by Baron von Trützschler-Falkenstein in Muggelsheim near Kopenik.

5. *Dualin.*—This was invented by Dittmar and is a mixture of nitro-glycerine with sawdust, or wood material from paper factories, previously treated with a mixture of nitric and sulphuric acids, or only impregnated with a solution of potassium nitrate

Dualin is a yellowish brown powder with a specific gravity of 1·02 In the open air it burns without exploding. Yet it is more sensitive to blow, shock, and fire than dynamite and lithofrakteur. In particular it was observed that on boring out the cartridge for the purpose of inserting the percussion cap accidents occurred. Now special fuse cartridges are supplied which are hollowed out for the reception of the capsule.

Ignition of dualin is best obtained by means of a strong percussion cap, but in a dry place and with solid tamping a fuse would be sufficient.

Dualin cartridges are covered with water-glass in order to protect them against damp.

The disadvantages of dualin as compared with dynamite consist in the greater danger attending its manipulation and its lesser specific gravity, the charges taking up much more space, and accordingly the bore holes have to be made much wider. Also wood fibre is not such a good absorbent as kieselguhr and therefore stronger cases are necessary.

Sebastin and serranin explosives are, probably, similar mixtures to dualin.

6. *Cellulose Dynamite.*—This was invented by the former K.K. Austrian Engineer-in-Chief J. Trauzl, and has as absorbent of nitro-glycerine specially prepared wood fibre material. It combines all the advantages of kieselguhr-dynamite with the advantage of gun cotton of being insensitive to water. The peculiarly treated wood material is a thoroughly suitable absorbent, which absorbs 70-75 per cent explosive oil.

This explosive in contact with water remains stable in composition, and after pressing out and drying, regains its former power.

7. *Dynamites 2, 3, and 4.*—These are mixtures of saltpetre and carboniferous substances (as boring dust) which serve as absorbents of nitro-glycerine. They are weaker than gelatine-dynamite, kieselguhr dynamite No. 1, and cellulose dynamite.

The composition of these dynamites is given as follows:

	No. 2	No. 3	No. 4
Nitro-glycerine . . .	60	70	50
Kieselguhr	10	--	
Wood material . . .	10	20	15
Barium nitrate . . .	20	10	35

On remaining some time in water the nitro-glycerine separates (as in the case of dynamite No. 1), and the absorbent (saltpetre and boring dust) is rendered incombustible and non-explosive. If exposed to the action of the water for only a short time, as is mostly the case in mining, it remains quite unchanged.

All charges of dynamite 1, 2, 3, or 4 which are used under water should be protected by waterproof casings. This is not necessary in the case of gelatine dynamite and cellulose dynamite.

The more dynamites 2, 3, and 4 contain of the absorbent and the content of the latter increases as the number goes higher, while on the other hand that of the nitro-glycerine decreases—the stronger is the action in an explosion. Consequently, the strong kinds of dynamite Nos 1 and 2 have a more breaking, and the weaker kinds of dynamite Nos. 3 and 4 a more crushing action, similar to powder.

It is just this gradation in the action of the dynamites 1, 2, 3, and 4 which renders their use so valuable. The cases in which, in the practice of blasting, dynamites 1, 2, 3 or 4 should be applied, are accurately indicated by the kind of action it is desired to produce.

8. We now come to those dynamites which are produced by amalgamation of gun cotton, collodion cotton, with nitro-glycerine.

Trauzl has conducted experiments with gun cotton impregnated with nitro-glycerine and which is known under the name of gun-cotton dynamite. He found that this mixture, which can be handled and stored without any danger, has a highly explosive action, with a water content of 15 per cent, if ignited with a strong fuse (match). A mixture of 73 parts nitro-glycerine, 25 parts of gun cotton, and 2 parts of carbon, after immersion in water for four days absorbed 15 per cent of the latter, but could, however, be made to explode easily with a strong fuse.

The manifest advantages of this gun-cotton dynamite resulted in an attempt being made to produce an explosive composition with collodion cotton and dynamite. In this manner explosive gelatine (gelatine dynamite) was discovered, which was destined to bring about a great improvement in the production of explosives.

The production of explosive gelatine is based on the fact that the lower cellulose nitrates such as the collodion cottons containing 8 and 9 nitro groups are soluble in ether. As nitro-glycerine is also an ester, then collodion cotton will be dissolved by it. Consequently, collodion cotton forms a most perfect absorbent for nitro-glycerine; it is itself practically an explosive, but it also modifies considerably the properties of dynamite. One-half per cent of collodion cotton is sufficient to convert the nitro-glycerine into a thick, jelly-like mass, and 8 per cent, as is generally used for the production of explosive gelatine, enables the production of a tough, solid, and horny like body which can be cut with a knife and moulded, whereas the best kieselguhr can only absorb at the most 80 per cent of nitro-glycerine.

For the preparation of explosive gelatine, nitro-glycerine is heated in copper pans and nitrated cotton is mixed with it by hand until a solid mass is formed. This remains from three to six hours in the pans, until the mass has taken on an entirely transparent appearance, the water under the pans which has served for heating from 90°-97 being continually changed during this time. It is then stored in a room heated to 50°. After this the gelatine is placed in specially constructed presses where it is formed into sausages, and it is treated in the same way as the dynamite. In order to render it insensitive to violent shocks—for instance, gun-shot—it is given an addition of camphor for war purposes. Of course, in this case special fuse cartridges are necessary for explosion purposes. In the place of camphor, pitch, resin, aniline, diphenylamine, tannin, etc., have been proposed.

Generally explosive gelatine is composed of 92 per cent nitro-glycerine and 8 per cent collodion cotton. Sometimes a small percentage of the latter is replaced by saltpetre.

As explosive gelatine, when stored, sometimes allows the nitro-glycerine to ooze out, and is of no particular stability, gelatine dynamite is mostly used for blasting purposes.

Gelatine Dynamite is manufactured from nitro-glycerine and about 3 per cent collodion cotton by heating the former in copper pans with water at 97 up to 50° or 60°, and then the nitro-cellulose is mixed in by hand. After an hour's heating, a syrup-like mass is formed with which the zunic powder, composed of saltpetre, boring dust, and soda is amalgamated. By means of a sausage machine with a driving screw, the gelatine dynamite cartridges are formed.

For the production of gelatine dynamite special kneading machines are employed, the construction of which is shown in Fig. 6 (p. 241). It consists of a wooden frame *a*, on which a false bottom *b* can by means of two screw shafts *c* be moved higher or lower. These catch with nuts *d* into the side walls fitted into the base and continue upwards in plain shafting to which a bevel wheel *e* is fixed. A shaft F fixed above the apparatus by means of two counter bevel wheels catches into the shafts. By turning the crank *h* the false bottom is raised On it there is a copper pan *i* on four wheels with a water jacket *j*. At the top the wooden frame carries a second shaft *k* with a fly wheel, two discs *m*, *n* and two bevel wheels *o*. These catch into the counter-wheels *p* which are fixed to two shafts *q*, carrying finger-shaped mixing wings *r* placed cross-wise. The work is then carried on in such a manner that the axle with the double pan is pushed on to the false bottom, where by *j* it is warmed to 40°-50° C., and pushed upwards until the wings dip, and these are then set in motion After about an hour the operation is finished Also the well-known Werner Pfleiderer kneading machines are used.

Gelatine dynamite No. 1, which is generally used for blasting work in Germany, is composed as follows :—

Per cent.	Per cent.		Per cent.
65 Gelatine	96·15	Nitro-glycerine .	62·50
	3·85	Collodion cotton	2·5
35 Zumic powder	75	Sodium nitrate .	26·25
	24	Sawdust . .	8·40
	1	Soda . . .	0·35
			100·00

This gelatine dynamite is called "Gelignit".

In England gelatine dynamite is prepared with 80 per cent gelatine and 20 per cent zumic powder.

The weaker kinds of dynamite, Nos. 2 and 3, are composed of—No 2, 45 per cent gelatine and 55 per cent zumic powder; No. 3, 14 per cent nitro-glycerine and 86 per cent zumic powder.

Zumic powder is prepared in the following manner:—

70	per cent	Sodium nitrate
15	,,	Sulphur
14	,,	Charcoal
1	,,	Soda

Particularly strong dynamites are obtained by an addition of ammonium nitrate, as for instance ammongelatine, extradynamite, etc., etc.

We have now only to mention briefly different dynamites which are used in blasting operations or are recommended for use. They belong to the class of dynamites with chemically active absorbent, but cannot well be placed in any one of the three subdivisions given above. They are:—

Fulminatin, invented by Justus Fuchs (in Alt Berau in Silesia), which is a mixture of nitro-glycerine with a combustible organic substance (presumably shearing wool).

Pantopollit, composed of 20-23 per cent infusorial earth; 2-3 per cent chalk; 7 per cent heavy spar and up to 70 per cent of a solution of naphthalene in explosive oil. This explosive was manufactured by a Rhenish factory at Opladen. The naphthalene was said to arrest the unpleasant fumes resulting from the explosion. The explosive effect was good; however, the smoke and smell resulting from the discharge of the shot was so unpleasant that the workmen at once complained of violent head and chest pains and for a long time could not continue their work

Rhexit, invented by C. Diller, contains 64 per cent nitro-glycerine, 11 per cent wood pulp, 7 per cent wood dust, 18 per cent sodium nitrate.

Meganit of Schuckher & Co., composed of 60 per cent nitro-glycerine, 10 per cent nitrated wood, 10 per cent nitrated brazil nut, and 20 per cent sodium nitrate.

Karbo Dynamite of Reid and Borland—90 per cent nitro-glycerine, 10 per cent cork charcoal.

Karbonit of Schmidt and Bichel—25 per cent nitro-glycerine, 40·5 per cent wood dust, 34 per cent sodium nitrate, 0·5 per cent sodium carbonate.

Stonit of Schmidt and Bichel—68 per cent nitroglycerine, 20 per cent kieselguhr, 4 per cent wood dust, 8 per cent potassium nitrate.

Dynamite of Vonges (France)—75 per cent nitro-glycerine, 20·8 per cent randonite (weathered felspar), 3·8 per cent quartz, 0·4 per cent magnesium carbonate.

Hercules Powder (America)—40 per cent nitro-glycerine, 45 per cent sodium nitrate, 11 per cent wood substance, 1 per cent kitchen salt, 1 per cent magnesium carbonate.

Vulcan Powder (America)—30 per cent nitro-glycerine, 52·5 per cent sodium nitrate, 7 per cent sulphur, 10·5 per cent charcoal

Safety Nitro-Powder (America)—68·81 per cent nitro-glycerine, 18·35 per cent sodium nitrate, 12·84 per cent wood substance.

Judson Powder (America)—5 per cent nitro-glycerine, 64 per cent sodium nitrate, 16 per cent sulphur, 15 per cent cannel coal.

Atlas Powder (America)—75 per cent nitro-glycerine, 2 per cent sodium nitrate, 21 per cent wood fibre, 2 per cent magnesium carbonate

Vigorit (America)—75 per cent nitro-glycerine, 4 per cent potassium chlorate, 7 per cent potassium nitrate, 9 per cent wood substance, 5 per cent magnesium carbonate.

In addition, particular mention should be made of the so-called " weather dynamites ".

The fire-damp in coal-mines is a mixture of mine gas (Methane CH_4) with at least 6 parts of air; mixtures with more mine gas are not explosive. If such a gas combination is ignited, it burns with a fearful explosion, and this, unfortunately, claims an increasing number of victims every year. Coal-dust, moreover, if in the air in a finely divided state, is easily set fire to, and the combustion spreads quickly and takes on the character of an explosion. The combustion of such substances can also be brought about by blasting operations as well as by careless handling of the mine lamps Therefore, in those mines in which there is the danger of fire-damp, or of coal-dust explosions, the ignition of the dynamite charge should only be accomplished by means of electricity, and, then, direct exploding substances, such as powder, etc., should not be used, as these burn too slowly, whilst the coal begins to free itself, and as long as there is a portion of the charge in the bore hole, the open combustion thereof can cause an explosion. Therefore, only explosives such as dynamite of the strongest kind should be used, then the danger is very considerably minimized, and by careful choice of the charge, the drawback of the too violent shattering of the coal is avoided. Mallard and Le Chatelier found, further, that all explosive materials, the ignition temperature of which were under 2200°, did not ignite fire-damp. To these explosives belong all those which contain ammonium nitrate in large quantities, such as roburite, ammon-gelatine, bellit, etc.

Finally, experiments have been made—apart from the proposals of filling the bore-holes with water, or putting the cartridges in cases filled with water or sand, in order thereby to avoid contact of the air with the explosive flame—mixing with dynamite soda crystals or sodium sulphate, the large amount of water of crystallization vaporizing in an explosion and forming a sort of water jacket.

These weather dynamites are of the following compositions:—

Nobel's weather dynamite:—

Nitro-glycerine	52 per cent
Kieselguhr	14 ,,
Soda crystals	34 ,,

Ammon-weather dynamite:—

	I	II	III.
Nitro-glycerine . . .	60	50	40
Sal ammoniac . . .	40	50	60

These kinds are less certain than soda-weather dynamite, and in an explosion develop unpleasant sal ammoniac fumes

The former applies also to

Kubin's Weather-dynamite:—

	I	II.	III
Nitro-benzolgelatine . .	30	42	40
Ammonium nitrate . .	40	8	—
Ammonium sulphate . .	30	—	50

The following composition for weather dynamites has proved thoroughly reliable, as even when using 1000 g. no explosion resulted:—

Guhr dynamite:—

	I	II.
Explosive Oil . . .	45	40
Kieselguhr	12	10
Magnesium sulphate	42	19
Soda	1	1

Gelatine dynamite:—

	I	II
Explosive oil	38·5	25
Zumic powder	18	10
Magnesium sulphate	42·5	64
Soda	1	1

A drawback, however, of all these dynamites consists in the fact that through the addition of soda, that is, owing to the water of crystallisation in the soda having to be vaporized, the explosive action is somewhat lessened. Such dynamite might, therefore, be too expensive in comparison with ordinary strong dynamite, the use of which as a rule offers the same security.

Ammongelatine dynamite contains:—

Nitro-glycerine	25-30 per cent
Collodion cotton	1 ,,
Flour (meal)	10 ,,
Ammonium nitrate	40-45 ,,

These dynamites are much in use, and by the addition of cooking salt the security against ignition is increased.

CHAPTER IX.

LEAD GLYCERIDE (GLYCERINE CEMENT).

It has been known for some time that glycerine which has been intimately mixed with protoxide of lead (litharge) results in a mass which, after a short time, becomes as hard as stone and can be employed for many useful purposes, but particularly for the production of very resistant cements. It was first ascertained by experiments carried out by Morawski that glycerine with protoxide of lead formed a combination of a definite constitution—lead glyceride. The lead glyceride which results from the mixing of glycerine with protoxide of lead, is of the following composition $C_3H_5(HPbO_3) + H_2O$ and is crystalline. The crystals can be obtained in quite a pure form, that is, in the shape of very small needles, if to a solution of protoxide of lead in potash-lye glycerine is added.

The behaviour of glycerine cement on treatment with chemical reagents was tried in such a manner that parallelipipeds of 3 mm. thickness were made of the cement and submitted to the action of different reagents. Concentrated and diluted acetic acid easily dissolved the cement after three hours' action;

concentrated nitric acid attacks it very slightly, as the lead nitrate which is so difficult to dissolve hinders the further action of the acid; diluted nitric acid easily causes the dissolution. Concentrated and diluted sulphuric acid (1 : 4) behave in the same manner as nitric acid. Muriatic acid, diluted as well as concentrated, has scarcely any effect on the mass; potash-lye soon disintegrates the composition; ammonia solution hardly affects it.

In order to ascertain the most favourable conditions for the production of the cement between protoxide and glycerine, bars were prepared from different mixtures of the two substances and water, of exactly similar size (25 mm. long, 11 mm. wide, and 3 mm. thick), and their solidity determined by supporting them at each end and applying weights in the centre until they broke. The table on next page gives the results of these experiments.

A mixture of 50 g. litharge and 5 c.cm. of glycerine results therefore in the most solid cement; but it is difficult to make, as hardening sets in before the mixture has been sufficiently mixed by mechanical means. It is more easy to make such a cement by mixing 5 volumes of glycerine with 2 volumes of water and of this liquid mix 60 c.cm. with 50 g. of litharge.

This mass very rapidly hardens and after ten minutes is already fairly hard, and after three hours harder than any other; in the course of time, however, it is exceeded in hardness and solidity by the cement prepared according to Experiment 9.

No.	Dilution of Glycerine. Vol. of Glycerine to Water	c.cm. per 50 g. lead oxide	Behaviour on hardening.	Breaking Weight.	
				Grammes.	After days.
1	10 : 60	6	Is not a good hardening mass; scarcely coherent.	-	-
2	10 : 40	6	Somewhat harder, but easily crushed between the fingers.	-	-
3	10 : 30	6	Distinctly harder than 2, but not yet satisfactory		
4	10 : 20	6	After standing for several days, can still be easily cut.	550	4
5	10 : 10	7	More solid than 4 but less so than 6		-
6	10 : 10	5	Distinctly more solid than 5. In the form of small, slightly resonant plates, quickly sets, difficult to mix		
7	10 : 6	6	Fairly hard, and already shows a clean cut.	800	4
8	10 : 4	5	Hardened in 10 min., after 2 hours very solid, difficult to mix.	1700	4
9	10 : 4	6	After 2 hours more solid than any other mass, hardens just as quickly.	2020	4
10	10 : 4	7	In 10 min. tenacious and binding and in 2 hours very solid.	1550	4
11	Conc. glyc.	7·5	After 3 hours not sufficiently hardened, but in a few days fairly hard.	1100	4
12	"	7	The same almost as 11.	1020 1750	3 6
13	"	6	Hardens in a shorter time than 12 and is more solid.	2070 1540	3 6
14	"	5	After 10 min. already particularly tough and in 20-30 min. is solid.	3080	6

The glycerine cement is a yellow or brownish mass, which, pressed into moulds and left in these for some days, fills out the finest hollowings of the mould, and is, therefore, very suitable for coin impressions or reliefs, which are more solid than plaster or cement casts.

The cement is particularly suitable as foundations for objects which are of considerable weight, and which are, therefore, constantly subjected to blows, for this cement, in spite of the hardness it gains in course of time, never loses all its elasticity. Foundations of steam engines, stamping machines, etc., have therefore been made of lead-glyceride which is also used for cementing stones. In order to cement stones, the spaces in question should be smeared over with concentrated glycerine, then litharge should be powdered on to them, and the stones tightly pressed one on the other and for some days kept under pressure.

CHAPTER X.

GLYCERINE AS SOFTENING SUBSTANCE.

Owing to its high boiling-point, glycerine in itself belongs to those substances which evaporate with great difficulty; but it also possesses considerable hygroscopic qualities, that is it absorbs water from the air or from those bodies with which it is brought in contact. Therefore, if a wide vessel containing glycerine is exposed to the air, the liquid therein is increased because glycerine draws water from the air

If, then, a substance which, when exposed to the air on drying becomes hard and brittle, is mixed with a suitable quantity of glycerine, it can be kept soft and supple for any desired length of time, and should the substance in question be subject to decay, decay can be arrested if glycerine is present in large quantities. If glycerine is used in small quantities only, decay of the substance in question can also be prevented if in the glycerine an antiseptic substance, such as carbolic acid, boric acid, salicylic acid, be dissolved.

Glycerine for the Preservation of Furs, Stuffed Animals, and Animal Skins.

A raw animal skin on being exposed to the air dries, as is known, to a brittle hard mass; should the temperature be so low that the evaporation of the water does not take place rapidly enough, then the skin does not dry, but decays.

If raw animal skins are repeatedly rubbed with glycerine, then, after long exposure to the air, they not only do not decay, but retain their suppleness; in the case of heavy animal skins the suppleness is even increased by glycerine, and the simple process of rubbing these raw animal skins with glycerine would undoubtedly be the simplest tanning process, but for the fact that the application of glycerine for this purpose is precluded on account of its solubility in water.

For instance, if a skin which has been rendered supple by impregnation with glycerine were plunged in water, owing to osmosis there is an exchange between the liquid contained in the tissue of the skin and the liquid outside, and in this manner the glycerine is extracted again.

If, therefore, glycerine cannot be considered as a means of tanning in the real sense of the word, yet it can be used with extraordinary advantage in certain cases for the preservation of animal skins. Furs, and notably valuable furs, are mostly obtained from small animals (martens), and only tanned with difficulty on account of the great care to be exercised in connection with the hair.

In most cases people are content with rubbing the flesh side of the fur with alum and cooking salt, and accordingly give it a superficial white tanning. Furs treated in this manner have, however, two drawbacks—the skin, in spite of the fact that it is not very thick, is brittle, because softening thereof by mechanical means (fulling) can not be resorted to, owing to the care with which the hair side must be treated; or it cannot be proceeded with in such a manner as to render the skin quite supple. The second drawback, which in the case of some furs is noticeably unpleasant, is the smell peculiar to the animal from which the fur is obtained.

Both drawbacks can be remedied in a very simple manner, if the preservation of the fur is accomplished by means of glycerine, and this is carried out in the following manner:—

The skin is first placed in water in order to render it supple, and is then washed in either a soap or soda solution in order to remove fat or dirt and to conserve the hair side in all its beauty. After this treatment the fur is repeatedly rinsed in water and is then placed, the hair side downwards, on a table and the flesh side is then manipulated with the instruments as used by tanners for this purpose and all particles of flesh and all hard lumps in the skin removed

After completion of this work, the skin is rubbed on the flesh side with concentrated glycerine, in which boric acid has been dissolved; this rubbing is repeated two or three times and the skin is then hung in a room to dry. By means of the washing process, the skin is thoroughly soaked through and through with water; as soon as the concentrated glycerine is applied to the flesh side of the fur, the action of osmosis sets in and the whole skin is then impregnated with a diluted solution of glycerine corresponding to the water contents thereof.

If the skins hang in dry air, then the water is allowed to evaporate until the glycerine is so concentrated that no more water escapes; the whole tissue of the skin is now so impregnated with glycerine that it will always remain supple, and is thoroughly protected against decay by the strong antiseptic action of the boric acid.

In order to mask the faint smell which some furs even after repeated washing do not lose, instead of ordinary glycerine, such glycerine should be used as is slightly perfumed with a not too volatile sweet-smelling substance such as ambergris or nutmeg oil.

The fur treated in this manner, on the flesh side has the appearance of a fresh skin; if it is desired to impart to it the appearance of tawed leather, this can be accomplished in a very simple manner by spreading over it a cold solution of alum or aluminium sulphate, leaving it to dry and then dabbing it over with a sponge dipped in ammonia. In this way the aluminium hydroxide is separated from the flesh side of the skin, which thereby has the appearance of tawed leather.

In the same manner as for furs can be treated the skins of animals, which are to be stuffed, such as birds, and this process is particularly valuable for naturalists when travelling, who are not able to stuff immediately the skins of animals and birds caught. If the fresh skins are treated with glycerine in which for this purpose salicylic acid instead of boric acid has been dissolved (on account of its powerful preserving action) then the skins or birds can, as soon as they are dried, be packed in boxes and left there as long as desired. If the bird is to be stuffed, then it is quite supple and much trouble is saved which would be otherwise occasioned by the softening of the dried and stiff skin.

GLYCERINE FOR THE PRESERVATION OF WHOLE ANIMALS.

Glycerine is also of importance to the naturalist from another point of view, and therefore we touch on its value for natural history purposes. It is known that some animals preserved in alcohol become irrecognizable in the course of time, because the alcohol dissolves the fat in the body and destroys the colour. This is particularly noticeable in the case of some beautifully coloured sea worms and fish which shrink in alcohol and entirely lose their colours. We have found that glycerine which is sufficiently diluted with water, in order that the very watery bodies of worms and other molluscs as well as of fishes should not shrink by the absorption of the water, is eminently adaptable for the preservation of such animals. For this purpose we prepare a preserving fluid according to the following method: -

Glycerine	200 g.
Water	800 ,,
Salicylic acid	4 ,,

The glycerine and water mixture is placed in a bottle into which the powder like salicylic acid is shaken, and for a week the bottle is shaken several times a day.

The salicylic acid, which is more easily dissolved in a liquid containing glycerine than in water, dissolves in the diluted glycerine, and this after it has been filtered can then be used for the preservation of animals.

The use of this liquid for the preservation of animals has the following advantages: The animals remain completely preserved in shape and colour, both the glycerine and the salicylic acid protect them against decay. The preserving liquid does not evaporate very much, and therefore the sealing of the vessels is not so troublesome as in the case of preparations preserved in alcohol. If a vessel is so badly closed that after a short time a noticeable quantity of the preservation liquid has evaporated, then all that is necessary is to replace the evaporated liquid by clean water and to hermetically seal the vessel. Formaldehyde (formalin) can be substituted for salicylic acid.

GLYCERINE APPLIED TO MICROSCOPY.

Glycerine is also eminently suitable for purposes of microscopy, not only for the production of microscopic preparations which are to be preserved for some time, but also for the purposes of observation under the microscope.

As a liquid of very strong light-refracting properties, glycerine can be used with advantage in connection with preparations which are to be observed in transmitted light, but which do not possess the required degree of transparency to allow the satisfactory passage of the light.

For this purpose only one drop of glycerine need be placed on the stand and the object to be placed under observation should be dipped in the glycerine If the object is a tissue containing water, it is all the same whether of animal or plant origin, the glycerine owing to the action of osmosis fills the cells and vessels in a few seconds and in this manner microscopic preparations are obtained.

If the preparations are soft and contain much water, the glycerine to be used should not be too concentrated, as it may easily happen that on account of the water-absorbing quality of the concentrated glycerine, the soft parts of the preparations may be altered.

For the preservation of microscopic preparations glycerine is much used; the object in question is placed on a glass plate furnished with a ring of microscope lac, and by means of a glass rod dipped in glycerine a drop of the liquid is placed on the object and it is then covered in the usual manner with a glass cover.

As glycerine never dries, and at the same time prevents decomposition of the object, this simple artifice will suffice to preserve the most delicate plant and animal preparation without any alteration whatever

In a still more perfect manner these microscopic preparations can be preserved by enclosing them in glycerine gelatine, and we will demonstrate this process when discussing the preparations made of glycerine and gelatine.

GLYCERINE USED IN THE MANUFACTURE OF LEATHER.

In the manufacture of leather, and particularly in those branches thereof dealing with the manufacture of chamois and tawed leather (*glace* leather), several liquids are used which have the object of imparting to the leather that high degree of suppleness which is required in the case of chamois and tawed leather.

For the purpose of chamois leather tanning, a liquid is used which is known as "degras". A part of this degras is obtained by endeavouring to extract from the leather treated with oil, the excess of oil, this is done by fulling; another part, and the greater, is obtained by boiling grease in a solution of potash or soda, and constantly stirring the mixture. The solutions of potash or soda have the quality of bringing the grease into emulsion without disintegrating it. The grease is divided into very fine drops which float about in the liquid and give it a milky appearance.

By repeated treatment with degras, a certain degree of suppleness is given to chamois leather, and presence of alkaline substances prevents any specific odour due to rancidity, as the free fatty acids resulting therefrom are at once bound. In spite of this, chamois leather has a characteristic smell, very probably due to small quantities of volatile fatty acids which cannot be bound by the alkali.

As the application of degras only results in the suppleness of the leather, this preparation can be entirely substituted by glycerine: one application of glycerine to the chamois leather (it must be rubbed in as long as the leather is wet) quite does away with the treatment with degras; the leather is hereby rendered supple, without after some time assuming a strong odour or darkening, as is more or less the case with leather which has been treated with degras.

For this and other similar purposes there is no need, as will be seen, to use highly purified glycerine which is absolutely colourless and odourless, but a product may be used that has simply been obtained by means of distillation, and which does not need to be colourless and odourless. With regard to the latter quality, it must be remarked that there should be no smell of acrolein, as this substance even when largely diluted has a very objectionable odour.

In the manufacture of tawed leather, so-called alum leather and *glace* leather, degras is substituted by the so-called "food". This consists of several very dissimilar substances; fermented grain (groats) and bran are very often mixed with grated calf's brain and the skin is then impregnated with this "food".

In the manufacture of *glace* leather a similar "food" is more often used which contains yoke of egg The doping of skins tanned with alum is accomplished by treading with the feet or kneading with the hands in a flat vat filled with the "food".

Chemically, the brain and yolk of egg show a certain similarity because both substances contain a certain quantity of glycerine in addition to the fat, in the form of glycero-phosphoric acid, and in these cases in addition to the fat it is the glycerine which imparts suppleness to the leather.

The "doping" which consists of yolk of egg is fairly expensive, therefore manufacturers of bleached (tawed) *glacé* leather must sell the white of egg which comes away with the yolk, either to printing works or to manufacturers of albumen. As also in this case it is the glycerine to which the action of the doping belongs, this substance can be easily substituted for the yolk of egg.

Glycerine can best be applied by spreading the tanned skin out on a table, so that the side to be dyed should be underneath, and the other side is then lightly run over with a brush dipped in glycerine. Each two skins are placed with the brushed sides together, and a weight is placed on the skins and they are left for a few days.

During this time the glycerine is evenly absorbed by the whole mass of the leather and attains thereby the highest degree of suppleness. During the process of dyeing by painting or by means of dipping, the skins lose part of their suppleness, and, therefore, a preliminary experiment should be made in order to ascertain in how far the glycerine should be diluted so that the leather may attain the necessary degree of suppleness.

It is, moreover, possible, after the *glacé* leather has been dyed, by rubbing glycerine in on the non-dyed side to give it the necessary degree of suppleness, and it needs only a simple experiment in order to determine the quantity of glycerine which is necessary to impart to the leather lasting suppleness and elasticity.

Glycerine is also of value to manufacturers of tanned leather because it imparts to this particular leather a high degree of suppleness. The vamps of boots which owing to faulty tanning are somewhat brittle, can be very much improved in quality and rendered quite supple. To this end the leather need only be spread with glycerine on one side, and, if necessary, this operation can be repeated once or twice.

A heavy red tanned leather such as is used for belts possesses the drawback that it has very little suppleness; a considerable portion of the power used to drive machines with belts is lost because the belts only turn round the wheels with stiffness. The edges also easily fray and after a time split.

These drawbacks can best be remedied by impregnating the belts with glycerine, which can be accomplished by repeated applications of glycerine, and by this means even very thick straps without in the least losing their firmness can be made so supple and durable that they even run round wheels of very slight diameter, without fraying or necessitating any particular expenditure of force as regards bending or stretching.

CHAPTER XI.

PREPARATIONS OF GLYCERINE AND GLUE.

GLUE in a perfectly dry state forms a very hard and uncommonly brittle mass, which in contact with water for some time swells more and more and finally is transformed into a very voluminous and soft jelly, which on slight heating melts into a solution of glue in water.

The high degree of elasticity possessed by glue which has absorbed a certain quantity of water would render it very suitable for some purposes, if the steeped glue did not putrefy so quickly. This could indeed be prevented by adding to the water in which the glue is steeped a powerful preservative (for instance salicylic acid), but even in this case it would not be possible to obtain an elastic mass of permanent uniform quality because the glue is constantly letting water evaporate, and therefore become less voluminous and elastic and finally would dry up to a hard brittle mass again.

By the addition of a suitable quantity of glycerine it is possible to impart to the glue those lasting qualities of elasticity which are only transitory in the case of glue melted with water, and such glycerine glue can be used for quite a number of different purposes. According to the end in view, glue of different degrees of purity can be used; the most common joiner's glue and the finest colourless gelatine result in preparations of fairly similar qualities and only differ strongly from one another in colour.

The production of glycerine glue is best proceeded with in such a manner that the glue is first allowed to soak in water and the cakes are transformed into soft flaky masses, which on lifting can easily be torn, the water is then poured off, the steeped glue carefully melted and boiled when all the scum which appears during boiling floats on the surface and is removed.

After this the necessary amount of glycerine is added, and by stirring is intimately mixed with the glue solution.

If a sample of glycerine glue prepared in this manner does not show sufficient firmness on cooling, then this is a proof that the mass contains too much water, and by careful evaporation the excess of water can be removed. The only precaution necessary to take in this connexion consists in constant stirring as soon as the mass begins to thicken in order to avoid burning, which easily takes place where the flame touches the vessel. If evaporation does not take place over an open fire but on the hob danger of burning is much less. Burnt glycerine glue has a dark colour and a peculiar sweet sort of smell.

If the evaporated mass is sufficiently firm, it is immediately poured into shapes ready to receive the mass, and they are left for a time until the entire mass is so hard that on touching it with the finger it does not stick.

If it is a case of making a light-coloured glycerine glue from dark glue, then, on soaking, the glue must also be cleaned. In the place of plain water, water to which a percentage of strong vinegar has been added may be used, and the first water is poured on to the glue only three hours later, the second and subsequent (4-5) waters at intervals of two hours.

Owing to this water containing vinegar, osmosis extracts from the glue a considerable number of salts and colouring matter, and in this way it is possible to manufacture from an evil smelling, practically black glue, glycerine glue which is the colour of dark amber.

GLYCERINE GELATINE.

This preparation, which is eminently suitable for the preservation of delicate microscopic preparations (see p. 140), is obtained as follows: The purest colourless gelatine is steeped in water for so long that, after the water is poured off, on heating it just melts at 100°. The steeped gelatine is placed in a glass, which is put in water and heated until it boils. As soon as the gelatine has melted, concentrated glycerine is dropped into the liquid and mixed by stirring with a glass rod, the mass is then poured into a china cup and left to congeal.

The addition of glycerine is so proportioned that the congealed mass on heating becomes liquid at about 50°; properly prepared in a solid state it is a perfectly transparent and colourless mass which has a certain degree of hardness.

If a microscopic preparation is to be preserved in glycerine gelatine, a small piece of the gelatine is placed on a glass plate, this is heated to 51°-53° and the preparation to be preserved is pressed into the melted glycerine glue, when care must be exercised that there are no air bubbles. After the plate has been left for some time the glycerine glue thoroughly hardens and the preparation is embedded therein, or melted, just as some firm objects are melted into glass.

It is of importance in the production of glycerine glue for microscopic purposes to take care that the preparation should be as firm as possible, which can be attained by avoiding any excess of water during the process; further, the melting-point should not be higher than 50°, which can be managed by proper regulation of the quantity of glycerine. To observe this condition as regards the melting-point is necessary, as in glycerine glue with a high melting-point delicate plant and anatomical preparations easily change owing to loss of water.

Glycerine-Glue for Printing Rollers.

Glue, used for this purpose, should be of a not too dark average kind, and is mixed with so much glycerine as seems necessary for the roller mass. Roller material intended for printing needs far less glycerine than the roller mass intended for the transmission of ink on to copper printing or lithograph plates, because, owing to the care which must be exercised in regard to the plates, no heavy pressure should be used, as in the case of ordinary letter type or wood-cuts.

The production of glycerine glue for printing rollers takes place in exactly the same manner as was described for the preparation of glycerine gelatine, naturally, less care is necessary in this case than would be necessary for that delicate preparation. If the sample taken from the roller mass, after being boiled for some time, seems too firm, the defect can be remedied by the addition of glycerine; if it is too soft it can be steamed, or a certain quantity of glue can be added which must have been soaked sufficiently for it to soften. Then the whole mass must boil again for a time in order to bring the freshly added glue into solution.

The moulding of the glue mass for printing rollers is accomplished in a simple manner, and to this end a simple device is used which consists of a turned cylinder perfectly smooth inside which along its length can be divided into two halves. The cylinder is closed with a raised bottom and at the top by means of a ring supporting a cross-piece. In the bottom there is a square opening, and also the cross-piece of the ring fitted at the top has a similar opening. Through these openings a four-sided rod of wood is pushed which is fitted at both ends with round turned handles. After the roller mould has been arranged in this manner and placed in a vertical position, the melted roller mass is poured in an even stream into the hollow of the mould, so that no air bubbles form, and it is then left for a time until the glue mass is quite firm when the mould is opened, the now finished roller taken out and any seams taken off with a sharp knife.

The four-sided rod which is surrounded by the glue cylinder serves as a support; if after much use the roller is not to be employed any more, then the ink attaching to the surface is removed, the glue mass taken from the wooden rod and again melted.

The roller-mass should be of such a quality that it will easily absorb the ink from the plate on which it has been distributed, and on rolling over letter type, copper, or lithographic plates, should impart it to these, if the ink smears, then it is a proof that the roller mass contains too much glycerine; if the roller does not impart sufficient ink to the printing type or to the plate, then it contains too little glycerine.

The same mass which is used for the manufacture of printing rollers can also be used for producing an elastic foundation for the inks employed on hand presses in printing works for printing certain patterns, and in this case the glue mass is poured into plates a few centimetres thick.

HECTOGRAPH BLOCKS.

The property of the glycerine glue mass to absorb the ink from certain surfaces and impart it to others under light pressure has been known for some time and made use of in printing works. If a printed piece of paper, which has just come from the press and the ink on which is still quite damp, is placed on an elastic foundation, and a clean printing roller rolled over it lightly, then the roller absorbs part of the ink from the paper; if this roller is then passed over a sheet of paper which has been damped, and which also has an elastic foundation, it imparts to the paper the ink and a fairly clear impression is obtained. If rolled over a second, third, etc., sheet of paper, further but increasingly fainter impressions are obtained from the roller.

Owing to the capacity of the glycerine glue mass to absorb colours from a foundation and to transmit it to others, it has been successfully used for the copying of documents, and the instruments, with the help of which such copies have been made, have been called hectographs (hundred "copiers"), as they enable up to a hundred legible copies to be taken.

That this should be possible is again owing to the wonderful quality of glycerine, and the ink with which the original matter to be manifolded is written must also contain glycerine, and the manufacture of such inks will be described later.

The glycerine glue masses, used in the making of hectographs, are obtained in the manner already indicated, and in recipes given for the making of hectograph blocks, it is often recommended to use the best gelatine. It is, however, quite superfluous to use very expensive gelatine, as with ordinary glue of a good quality, for instance, so-called size, hectograph blocks can be made which, as regards copying capacity, are equally as satisfactory as those made with the application of gelatine.

Hectograph blocks corresponding to all requirements can, therefore, easily be made by soaking the size in water, adding glycerine, and allowing the mass to solidify; the addition of glycerine should be so proportioned that on cooling a product is obtained having the consistency of a very soft vulcanized rubber, and which on touching seems somewhat clammy. If size is employed the hectograph block obtained has an amber- or honey-yellow colour.

These hectographs, before they are poured into the shallow metal vessels used for this purpose, should be warmed for some hours to such an extent that they just remain in a thin liquid state. During this process all the foreign substances contained in the glue, as well as those parts of the glue which only soften but do not dissolve, settle at the bottom of the vessel and, by slowly pouring off, the solution can be separated from the sediment.

As already mentioned, it is sufficient to impart to the glycerine glue such a consistency that it is similar to soft rubber, and it then depends only on the quality of the ink with which the original is written, as to whether several or only a small number of copies can be obtained. In general, however, it can be taken that a firmer and less elastic hectograph mass gives a lesser number of copies, all of which are very clear, whereas from a softer hectograph mass (that is containing more glycerine) more copies can be taken, the last ones of which, however, show fainter outlines.

According to certain prescriptions for the preparation of hectograph masses, a powder-like substance of a white colour should be added to the glycerine glue in order to obtain a milk white mass, which shows up the writing more clearly. Such substances are, for example, finely ground heavy spar and zinc white: but there is not much object in this because it is not a question of reading the writing transmitted to the hectographs but of reading the copies taken from it.

Moreover, the addition of such substances has certain drawbacks as to the clearness of the copies. Under all circumstances the clearest and most numerous impressions are obtained when the hectograph mass is composed of glycerine and glue only. We will now give some formulæ for the making of these hectograph masses:

SIMPLE HECTOGRAPH BLOCKS.

Size	100 g.
Glycerine at 28° Beaumé	500 ,,

B.

Size	100 ,,
Glycerine at 28° Beaumé	400 ,,
Water	200 ,,

CHROMOGRAPH MASSES

are hectograph masses with additions of white substances which enable the writing to stand out more clearly, and also facilitate the washing away of the characters. Heavy spar must be used either in the form of the finest powder, or, still better, very finely divided barium sulphate should be used, which can be obtained by means of precipitation of a solution of barium chloride with sulphuric acid and washing the deposit.

A.

Size	100 g.
Barium sulphate (wet) . .	0·5 l.
Dextrin	100 g
Glycerine	1000-1200 g.

Dextrin and size are dissolved together, then the glycerine, and finally barium sulphate added, and the mass is poured into moulds. If an insufficient number of copies results, or if the writing can only be washed off with difficulty, then a mass of the proper quality can be obtained by melting it again and adding glycerine.

B.

Size	100 g.
Baryta precipitate	0·5 l.
Glycerine	1200 g.

C.

The French Ministry for Public Works recommends the following:—

Glue	100 g.
Glycerine	500 ,,
Finest powdered heavy spar or cleansed kaolin	25 ,,
Water	375

HECTOGRAPH MASSES ACCORDING TO WORTHA.

Gelatine	100 g.
Dextrin	100 ,,
Glycerine	1000 c.cm.
Barium sulphate	80 g.

Hectograph sheets which are intended to be used only once can be obtained by pouring the liquid hectograph mass on to a smooth horizontally placed glass plate, and transferring it to porous paper before hardening, by pressing it and avoiding the formation of air bubbles. Paper and mass combine and can be drawn off. The surface of these hectograph sheets is very smooth, and for this reason it is eminently suitable for the transmission of writings, drawings, etc., with very fine lines.

CHAPTER XII.

GLYCERINE APPLIED TO THE MANUFACTURE OF INKS.

1. HECTOGRAPH INKS.

IN order to fix the characters on the hectograph mass for subsequent removal, inks of suitable quality must be used. These must be so constituted that they can be taken by the paper from the hectograph mass and adhere firmly to the surface of the latter. The particles of the ink should be so fluid that they are able to pass from the absorbing block on to the paper laid on it.

As the richest colouring matters are used for the production of hectograph inks, only a small portion of the colour is absorbed by the paper, and by laying on fresh sheets ink is again absorbed, so that, as already mentioned, hundreds of copies can be taken of an original. The later copies are of course always fainter and fainter, till finally no more copies can be taken, although the characters on the surface of the hectograph are still quite clear. As much of the writing has then been absorbed by the paper as is possible from the hectograph block; the attractive power exercised by the hectograph mass on the ink is just as strong as that exercised by the paper, and, therefore, no further copies can be taken.

In order to obtain good hectograph ink, two points must be taken into consideration—the colouring matter contained in the ink must be very intense and the ink should never altogether dry up as otherwise the mobility of the particles is paralysed. Therefore, for the production of these inks the strongest colouring matter is used; these are so-called aniline dyes (fuchsin, methyl violet, water-soluble blue, iodide green, etc.), in the form of concentrated solutions to which glycerine is added in order to prevent drying up of the ink.

Glycerine incorporated with the hectograph ink not only serves to keep the characters soft, but also acts as a solvent for the colouring matter itself, because only a few aniline colouring substances are directly soluble in water, but they easily dissolve in glycerine, particularly when it is warmed.

Therefore, in the production of hectograph inks, the best method is to place the weighed-out colouring matter in a china mortar, pour over it the requisite amount of glycerine, and mix the colouring matter with the glycerine by means of the pestle. After this has been done for some time, so that no grains are noticed in the mixture, the mortar is heated to 50°-60° C. and thereby the colouring matter is brought into thorough solution, as warm glycerine dissolves far more of it.

If aniline colouring matter soluble in water, for instance water-soluble blue (alkali blue), is used, then to the thick solution of the dye in glycerine so much water is added that a liquid results, the consistency of which is similar to that of a thick ink, and then the hectograph ink is ready.

If an aniline dye, insoluble in water, is used, for instance methyl violet, then the thick liquid solution in glycerine is diluted with water to the extent that it becomes as thick as syrup, and so much alcohol is then added as is necessary to produce an ink of suitable consistency. An excess of alcohol should be avoided for the reason that inks containing too much alcohol thicken so much in the process of writing, owing to the volatility of the alcohol, that it is not possible to write fine characters with it.

PRESCRIPTIONS FOR VARIOUS COLOURED HECTOGRAPH INKS

Thin blue inks :—

Water-soluble blue	10 g.
Glycerine	10 ,,
Water	50-100 ,,

These are made by simply warming the substances and stirring.

Violet hectograph ink :—

A.

Methyl violet	10 g.
Diluted acetic acid	5 ,,
Strong alcohol	10 ,,
Water	10 ,,
Glycerine	5 ,,

Owing to the acetic acid it contains, this ink spoils steel nibs and soon makes them blunt; a more suitable recipe for violet ink is the following:—

B.

Methyl violet	10 g.
Alcohol	10 ,,
Gum	10 ,,
Glycerine	15 ,,
Water	70 ,,

All the ingredients are placed in a long-necked glass flask, constantly shaken and warmed for two hours up to about 60° C., and then left to cool. After standing for some time the solution is poured off from the sediment.

Red hectograph ink:—

Diamond fuchsin	10 g.
Alcohol	10 ,,
Acetic acid	2·5 ,,
Glycerine	10 ,,
Water	70 ,,

The method of preparation is the same as in the case of the violet ink B.

Another recipe is as follows:—

Diamond fuchsin	10 g.
Alcohol	10 ,,
Glycerine	10 ,,
Water	50 ,,

This prescription in particular results in inks which give a large number of clear impressions.

Green hectograph ink is produced in the same manner as the other inks described, by adding water-soluble blue and picric acid to a liquid composed of alcohol, water, and glycerine.

Green hectograph ink :—

Water-soluble blue	10 g.
Picric acid	10 ,,
Alcohol (90 per cent.)	30 ,,
Glycerine	10 ,,
Water	30 ,,

According to whether more or less picric acid is used, a lighter or darker green is obtained.

Black hectograph ink :—

Nigrosin or aniline black is insoluble in water. In order to produce a black hectograph ink, methyl violet and nigrosin are mixed and then treated with alcohol and glycerine. A prescription which is recommended is as follows :—

Methyl violet	10 g.
Nigrosin	20 ,,
Alcohol	60 ,,
Glycerine	30 ,,
Gum	5 ,,

According to Buchhaister, black hectograph ink can be prepared in the following manner : —

Nigrosin	15 g.
Methylated spirits	40 ,,
Glycerine	100 ,,
Acetic acid	5 ,,
Water	500 ,,

The Höchster dye works recommend the following dyes for the preparation of hectograph inks :—

For violet inks .	Methyl violet and crystal violet
For green inks .	Brilliant green and malachite green
For red inks .	Fuchsin
For yellow inks .	Auramin

2. COPYING INKS

Copying inks are those inks which allow at least one very clear copy to be taken of the document written with them; these inks are mostly used in business, in those cases where only one copy of the document is needed.

The preparation of copying inks has been looked upon as very difficult of accomplishment; at the present moment, however, such successful attempts have been made that in a short time practically every ink can be transformed into a copying ink. A good copying ink should possess the property of drying slowly and when, after a time, a damp and porous sheet of paper is placed on the document, should so soften again that part of the ink is absorbed by the paper.

Formerly, copying inks were made by mixing with the ink, extract of logwood and grape sugar, two substances with very strong water-attracting qualities. This hygroscopic quality prevented entire drying of the characters, and therefore after a time a good copy of the writing could be taken.

By the application of glycerine, the production of good copying inks has been rendered a very simple matter, and every ink by the addition of glycerine can at once be turned into copying ink. The amount of glycerine to be used depends on the quality of the ink itself and on the length of time the ink is required to remain capable of copying.

The more glycerine added to an ink the longer will the documents remain damp, and the copying capacity is of longer duration. In order quickly to determine the requisite amount of glycerine for a particular ink, it is advisable to divide the ink into several equal parts—about a teaspoonful—the first part should be mixed with 6, the second with 10, the third with 14 drops of glycerine, etc. With each of these samples a line should be written on the same piece of paper, and then after a time a copy should be taken of this sheet of paper. The sample which results in the best copy is prepared in the right proportion, and then the whole mass can be mixed with the equivalent quantity of glycerine.

GLYCERINE COPYING INK.

Logwood extract	100	g.
Sulphate of iron	4	,,
Potassium chromate	1	,,
Indigo carmine	8	,,
Glycerine	10	,,
Water	500	,,

This excellent copying ink may be prepared by dissolving the logwood extract at the same time with the sulphate of iron and potassium chromate in water, and mixing with the solution the glycerine and indigo carmine. Glycerine, itself a liquid, has only a slightly thickening effect on the ink; this differs, therefore, advantageously from other inks in that very fine characters can be written with it, as it is sufficiently thin. In spite of this quality, copies can frequently be taken, as it penetrates very deep into the paper and remains damp for some time.

COPYING INK ACCORDING TO BÖTTGER

Böttger's composition for a copying ink is given as follows:—

Logwood extract	64 g.
Soda	16 „
Potassium chromate	2 „
Glycerine	64 „
Gum	16 „
Water	270 „

The logwood extract is dissolved at the same time as the soda in water, glycerine and gum are added and, finally, potassium chromate, dissolved in a very little water (hot), is added to the liquid and stirred, and it can at once be taken into use.

This copying ink is of such a capacity that we were able without using a press to take three copies of the original document simply by pressure of the hand; in the copying press, that is under strong pressure, another two good copies were obtained.

LOGWOOD COPYING INK.

Extract of Logwood	70 g.
Vinegar	1 kg.
Water	1 ,,
Sulphate of iron	40 g.
Alum	20 ,,
Gum	35 ,,
Sugar	60 ,,
Glycerine	4-6 ,,

Logwood copying ink according to Büchhaister:—

50	parts of	logwood extract
6	,,	oxalic acid
35	,,	alum, dissolved in
1000	,,	water (cold) and
10	,,	glycerine are added.

It is left to settle, boiled, and 60 parts of pyroxylic acid are added, and it is again clarified by settling.

BIRMINGHAM COPYING INK.

Solution of logwood extract	650 g.
Dextrin	30 ,,
Alum	33 ,,
Verdigris	0·25 ,,
Oxalic acid	2 ,,
Glycerine	7-21 ,,

The addition of glycerine is increased if the ink is to be used for copying after some time.

ALLFIELD'S COPYING INK.

For copying without the use of a copying press:—

Ten volumes of ordinary ink should be evaporated to six volumes and then over four volumes of glycerine should be added. By merely placing the copy paper thereon, the writing is copied, but very easily smears.

CHAPTER XIII

GLYCERINE AS A SOLVENT.

THE property of glycerine easily to dissolve a large number of substances which are only dissolved with difficulty otherwise, renders the application of glycerine of great use in many trades As has already been mentioned, when describing the qualities of glycerine, it possesses the property of dissolving easily so-called aniline dyes, which are mostly only soluble in strong alcohol, and this property finds extensive application in dye works as well as in printing works.

If, for instance, in printing works aniline dyes are to be used which are only dissolved in alcohol, certain difficulties, which are due to the volatility of the solvent, must be overcome, as owing to the volatility of alcohol the colour easily thickens, and then darker shades result than were originally intended.

This drawback can immediately be remedied, by substituting glycerine for the alcohol as the solvent of the aniline dye. In order to dissolve the colouring matter, first of all a small amount of glycerine should be poured over it in order to prevent the finely divided dye scattering as dust, so unpleasant in the case of very deep dyes, and the dye should be mixed with the glycerine to an even paste. This should be stirred constantly and as much glycerine added as is necessary to effect the solution, and then this solution can by stirring be intimately mixed with the thickening substance whether dextrin, gum solution, tragacanth mucilage, etc., which is used for the production of the colour, and a printing colour results which in addition to the advantage of remaining the same on drying, neither dries nor crumbles, and enables the printing of the particular dye on the tissue to be accomplished with great facility.

Prescriptions in connection with colour printing, consisting of dissolved aniline dyes, are very numerous and vary according to the shade of colour one wishes to obtain. An example of aniline pink is the following:—

I.

Fuchsin	0·12 kg.
Glycerine	1·00 ,,
Water	1·00 ,,
Gummi arabicum	0·84 ,,

II.

Albumin	3·50 kg.
Water	3·50 ,,

In dyeing works in which either yarns or already finished textures are to be dyed with aniline dyes, the dye is brought into solution by boiling with alcohol, and these solutions are used for dyeing in suitable dilution.

GLYCERINE FOR THE EXTRACTION OF PERFUMES.

A very important application of glycerine is in obtaining certain substances used in perfumery; the most important ingredients in perfumery are, as is well known, the essential oils found in sweet-smelling plants. The quantities of ethereal oils found in plants are so small in the case of the most valuable, and the separation of them accompanied with so many difficulties, that these oils belong to the most expensive substances known. Although certain plants containing these ethereal oils are extensively cultivated in certain districts (for instance in the south of France, in the surroundings of Cannes, Nice, etc.), the demand for genuine ethereal oils (violet, mignonette oil, orange flower oil, acacia farnesiana oil, etc.) obtained from flowers is so great that the exceedingly high prices which are asked for these oils are still rising.

Glycerine is an excellent means of obtaining sweet-smelling substances from blossoms of the most varied kinds, and particular stress should here be laid on the fact that glycerine is eminently adapted for the extraction of all sweet-smelling substances from parts of plants whether flowers, roots, wood, or fruit peels, because it is a solvent for all these perfumes.

The method used for the extraction of perfumes from flowers by means of glycerine consists in the following:—

The blossoms are collected in a fresh condition, and any green, leaf-like parts removed as far as possible; they are then placed in a vessel and concentrated glycerine is poured over them. With regard to the kind of glycerine to be used for this purpose, the greatest attention must be paid to the fact that only such glycerine is used which on careful examination is proved to be absolutely free from any odour.

The kind of vessels used for this extraction process by means of glycerine depends upon the scale of the work; on a small scale, pot-shaped vessels of good stoneware are used, and for the treatment of large quantities of flowers, wooden vats of corresponding size, the interior of which has been coated with paraffin, are used.

The paraffining of the wooden vessels is accomplished in the following manner: After the vessel has stood for some days in a dry room, the interior is coated with melted paraffin which has been heated to 150° C., and this coating is repeated for so long as the wood will still absorb paraffin. By this means the wood is protected against the penetration of any liquids, and vessels treated in this manner can easily be cleaned by washing and brushing with warm water.

It should be observed in this connection that when it is a question of paraffining wooden vessels for the purpose under discussion, great care should be taken that only an absolutely pure and, in particular, odourless paraffin is used for impregnation as, otherwise, the smell attaching to inferior paraffin may be imparted to the wood. The flowers in the vessel are covered with wooden covers pierced with holes; these are lightly weighed down with a stone, and so much glycerine poured into the vessel until it rises a few centimetres above the cover. As the flowers contain a good deal of water, the glycerine is strongly diluted by the water absorbed from these flowers, and the vegetable substance contracts.

This placing of fresh flowers into the vessel continues for as long as there is a supply of them; on adding fresh lots the wooden cover is removed, and the fresh flowers are evenly distributed on those already in the vessel, the cover is replaced again, and so much glycerine added until again it stands some centimetres above the cover.

When the vessel is full, it can remain standing until the further work is proceeded with, the portions of the plant being perfectly preserved by the glycerine and decomposition is not likely to set in. The time necessary for complete extraction of the sweet-smelling substances from the flowers by means of glycerine amounts to a few days, and, accordingly, a week after the last lot of fresh flowers has been placed in the vessel, the glycerine can be treated.

To this end, a wooden cock fixed at the bottom of the vat is opened and remains open for as long as glycerine flows out; if stoneware vessels are being used, these are turned upside down and the glycerine trickles out. This glycerine smells very strongly of the plant substance which was soaked in the vessel, and is also dyed with the colouring matter absorbed from the flowers, and carries away with it small particles of the petals, etc.

In order to obtain a clear solution, this glycerine which flows out of the vessels is filtered through a thickly woven cloth into the vessel destined for its reception. The particles remaining in the extraction vessels contain considerable quantities of glycerine which can be obtained by pressure. To this end the pap-like mass is poured into a sack of very strong and thick texture, it is tightly tied, and thoroughly pressed in a powerful spindle press. The liquid which is pressed out of these sacks is as a rule more deeply dyed than that which flows out voluntarily and is also filtered.

On filtering the glycerine containing these perfumes in solution, care must be taken that the work proceeds as rapidly as possible, as the air has an injurious effect on the aroma of the essential oils; therefore, once the work is commenced it should be carried through without interruption to the end.

The clear solution of these extracted substances in glycerine can then at once be used for the production of certain articles of perfumery; if, for instance, a suitable quantity thereof is mixed with a thoroughly neutral fat, a pomade is at once obtained which has the odour of the treated flowers in all their freshness; if soap, which has been cut into shavings, is mixed with this glycerine, and this mixture is milled by means of the well-known mixing apparatus, the result of this simple work is that some of the finest toilet soaps with exquisite aroma are obtained.

By a careful addition of water to this perfume solution in glycerine, the former can be diluted to a certain extent, without the liquid losing anything of its clearness; but if this addition of water goes beyond a certain extent the liquid commences to opalesce and on adding more water becomes sometimes quite muddy; the essential oils and other substances which are extracted from the flowers are only soluble in a liquid which contains a certain quantity of glycerine, and are therefore separated when too much water is added.

Solutions of aromatic substances in glycerine, diluted with water to a point approaching that at which turbidity sets in, still retain the fresh smell of the flowers and can be used for very fine toilet washing water. In order to proceed further with the dilution than is possible with water alone, as soon as the turbidity point is reached, strongly diluted methylated spirits at 10-15 per cent, which must be free from fusel oil, is added and this prevents separation of the essential oils.

But in many cases it is a question of obtaining these aromatic substances in an absolutely pure state, and in this connection the glycerine solutions are treated in the following manner:—

The glycerine which has been drawn off from the flowers and filtered is placed in large glass bottles, closed with corks which are most carefully fitted into the necks of the bottles. Before the glycerine is placed in these bottles, so much pure benzol is placed in them until they are filled with it to about one quarter of their volume and then so much glycerine is poured in until they are three quarters filled. It is of importance that the benzol should be poured in the bottles before the glycerine so that these bottles should be filled with the vapour of the benzol, and on adding the glycerine the greater part of the air which was contained in the bottle is forced out by the benzol.

After the bottles have been closed, they are well shaken, so that the glycerine mixes with the benzol, and this shaking is repeated daily several times. After several days the greater part of the aromatic substance has been dissolved in the benzol which floats on the glycerine (insoluble in benzol); the glycerine, however, obstinately retains part of the aromatic substances, which cannot be extracted even by repeated treatment with benzol.

The solution of aromatic substances in benzol is separated by pouring off from the glycerine, placing it in a distilling apparatus, and heating to the boiling-point of the benzol, when the latter distils over and the aromatic substances remain in the distilling apparatus. They still contain traces of benzol and these are removed by introducing a stream of carbonic acid divided into very fine jets, which carries away the traces of benzol in the form of vapour and leaves the aromatic substances quite pure.

In this manner aromatic substances can be obtained from hyacinths, violets, lilies of the valley and certain sweet smelling orchids of our woods, mignonette, roses, etc., in short, the most exquisite aromatic substances of the plant world can be obtained, and for this reason glycerine deserves the consideration of all those interested in the production of perfumes and particularly in obtaining essential oils from fresh flowers. It is a fact, however, that this process which, under certain circumstances, is so highly to be recommended, is hardly resorted to at all in practice.

Glycerine used in the Preparation of Cosmetics

Among the numerous preparations sold to the public under the name of "beautifiers" or cosmetics by perfumery manufacturers, glycerine ranks as one of the first, as, if properly applied, it possesses the quality of imparting to the skin brilliance, softness, and delicate colour.

The proper method of application of glycerine in connection with the care of the skin is not in a concentrated form, but diluted with a suitable quantity of water. If concentrated glycerine is brought in contact with parts of the body which are covered with delicate skin—for instance, the lips or finger tips, there is immediately a strong sensation of warmth due to absorption by glycerine of the water in the skin.

By the sudden absorption of this water, the skin is easily injured, the soft cells forming the tissue of the lip skin are killed, they shrink and peel off as soon as a fresh layer of skin is formed underneath. As, therefore, by the application of concentrated glycerine the skin is not preserved but so to say "killed," this preparation should always be diluted with water before application.

Most astonishing is the action of glycerine on a skin which has been strongly tanned by the sun; whereas it would otherwise take several weeks before a skin tanned by the sun is bleached again, the application of glycerine bleaches it in a few days.

The action of glycerine in most cases is easily explained by its wonderful solvent action on the most varied substances. Thus tanning of the skin by the rays of the sun is to be ascribed to a deposit of colouring matter in certain cells of the skin. If glycerine is rubbed into the skin, it penetrates very deep into the tissues and dissolves the colouring matter, by subsequent washing, the glycerine absorbed by the skin is removed for the greater part, and at the same time the dissolved colouring matter is washed away, so that in a short time the skin is bleached again.

Glycerine for cosmetic purposes can be prepared in various manners and made aromatic by mixing it, for instance, with orange-flower water, or with water and eau de Cologne, etc.; or also by mixing glycerine with aromatic flowers in the same way as has been described in the preceding section. All these additions are of no cosmetic value, this is to be attributed to glycerine alone: aromatic substances merely render the application of glycerine more pleasant.

As glycerine removes the colouring matter due to the action of the sun's rays, so it can also remedy certain blemishes of the skin which are also due to deposits of colouring matter, as, for instance, moles and freckles, and if it does not remove them altogether, at any rate they are diminished, as glycerine is a solvent for these colouring matters.

An already clear and delicate skin is enhanced both as to freshness and smoothness by the application of glycerine, a phenomenon which can be explained by the fact that the cells of the outer skin attain a higher degree of transparency owing to the action of the glycerine, and the faint pink of those parts under the upper skin is made more distinct.

For the softening of and rapid removal of horny substances in the skin, such as, for instance, are formed on hands owing to some unusual work, glycerine is eminently suitable, as after repeated rubbing of these thick horny cells of which these disfigurements are formed, much glycerine is absorbed, and consequently they become so soft that by scraping them with a file made of sharks' skin or with a blunt knife, the greater part of this horny substance can be removed.

Diluted glycerine is excellent for the hair and skin. Some people complain a great deal of dandruff, which is to be attributed to the dying of the upper layer of the skin. By washing the head with diluted glycerine this drawback is remedied in the case of many people, as owing to the water-attracting and softening action of glycerine, this peeling off of the upper skin is prevented.

We now give a number of prescriptions for the preparation of various articles of toilet in which glycerine plays an important rôle. Readers who may care to interest themselves further in the subject should read the work on "Cosmetics" by T. Koller, published by Scott, Greenwood, & Son, London.

GLYCERINE EMULSIONS.

A. Glycerine Creams:—

Glycerine	250 g.
Almond oil	400 ,,
Rose-water	350 ,,
Spermaceti	100 ,,
Rose oil	4 ,,
Wax	32 ,,

Wax and spermaceti are melted at a gentle heat, first of all the almond oil is added, then the glycerine mixed with the rose-water, and finally rose oil, which can be replaced by some other sweet-smelling oil or compound perfume. If the preparation is to be used in the summer, it is as well to increase the wax by half, for this imparts more consistency to the whole mass.

B. Glycerine jelly:—

Glycerine	1 kg.
Almond oil	3 ,,
Soap	150 g.
Orange oil	10 ,,
Oil of thyme	20 ,,

Soap is mixed with glycerine, then gradually the oil and finally the aromatic substances are added.

REMEDY FOR BRITTLENESS OF THE HAIR.

Glycerine	2 g.
Water	1 l
Rose-water	1 ,,

Colour pale red with cochineal.

KALODERM.

Wheat flour	2 kg
Almond paste	0·5 ,,
Orris root	0·5 ,,
Essence of rose	0·5 l.
Glycerine	0·2 ,,

are mixed to a paste, diluted with water, and then applied to the skin.

Pâte au Musc (for a hand wash):—

Powdered white soap	1 kg
Orris root	0·25 ,,
Starch meal	0·25 ,,
Oil of lemon	20 ,,
Neroli oil	10 ,,
Essence of musk	0·05 l.
Glycerine	0·40 ,,

Boil until it forms an even paste, then fill into flat porcelain jars.

Eau glycerinée aux cantharides (glycerine cantharides water):—

Ammonia *pura liquida*	100 g.
Tincture of cantharides	100 ,,
Rosemary water	8 l.
Glycerine	300 g.
Rose oil	20 ,,

The tincture of cantharides is prepared by digesting 50 g. of powdered Spanish fly (*Lytta-vessicatoria*) with 1 l. of strong alcohol. The caustic ammonia has the same cleaning and degreasing action as potassium carbonate; glycerine imparts to the hair softness and suppleness. The whole composition is very well combined, inasmuch as it has a cleansing effect on the hair and at the same time imparts softness.

Preparations which have been in use for years are glycerine jellies. These have the advantage over lanoline that they are more economical, but on the other hand possess the drawback of not being so quickly absorbed. Either tubes or glasses are filled with these preparations; in any case the latter are preferred as they are more easy to manipulate.

A good prescription for these glycerine jellies is as follows:—

Finest white tragacanth powder .	50 g. damped with
Alcohol	100 ,, and
Glycerine	200 ,,

and thoroughly shaken; then quickly mixed with 650 g. of water (warmed and distilled) and again shaken. Immediately a transparent jelly is formed which can at once be bottled.

GLYCERINE CREAMS.

A. Glycerine cream:—

Almond oil	1 kg.
Wax	70 g.
Spermaceti	70 ,,

GLYCERINE CREAMS—(*cont.*)

Glycerine	200 g.
Bergamot oil	20 ,,
Lemon oil	20 ,,
Geranium oil	20 ,,
Neroli oil	10 ,,
Cinnamon oil	10 ,,
Rose-water	500 ,,

B. Glycerine cold cream :—

Almond oil	1 kg.
Wax	130 g.
Spermaceti	130 ,,
Glycerine	250 ,,
Rose oil	10 ,,
Civet	2 ,,

PREPARATION OF HAIR PETROLEUM.

For the preparation of hair petroleum the following prescription is given :—

Best petroleum (American Kaiser oil)	5 kg.
Tincture of nettles (obtained from 2 kg. of nettle root, 7 kg. of alcohol, and 3 kg. of distilled water)	10 ,,
Glycerine	5 ,,
Alcohol	48 ,,
Distilled water	40 ,,
Essential oil for perfuming	2 ,,

The petroleum which has previously been perfumed is mixed with alcohol at 96 per cent, and both are heated almost to boiling temperature in order to obtain thorough mixing and solution. After this, distilled water is added to the solution and the remaining ingredients are added in the proper order.

Hair petroleum effects the solution of the fatty substances of the hair, and also loosens the thrown-off epidermis in the form of dandruff, and imparts to the hair brilliance and suppleness.

CHAPTER XIV

VARIOUS APPLICATIONS OF GLYCERINE.

GLYCERINE USED IN THE MANUFACTURE OF SOAP

SOAPS which are prepared according to the old process contain only very little glycerine; the manufacture of these soaps (curd soaps) is accomplished by saponifying the fat with lye previously obtained from wood ashes (potash lye), and the soap so formed is by the addition of cooking salt transformed into soda soap, and this, by adding an excess of cooking salt, is separated (salted out).

In this method of manufacture nearly all the glycerine which results from the decomposition of the fat goes into the lye underneath, and even now is often thrown away and not used These soaps which in stearic acid manufactories are obtained by saponification of the oleic acid with soda lye contain no glycerine on account of the method of preparation.

Since soap has been made by direct saponification of fat with concentrated soda lye, it has been possible to impart to it, in spite of the high contents of water, a sufficient degree of hardness, and therefore the whole salting out process can be dispensed with, by boiling the soap in the vessel for so long until a sample on cooling shows sufficient consistency.

Soaps made in this manner contain the total amount of glycerine in the fat originally used, and, therefore, have a beautifying effect on the skin, because the glycerine contained in the soap easily penetrates into the tissue of the skin and imparts to it softness and suppleness.

If to an ordinary soap (tallow curd soap) glycerine is added and the soap melted with this, the result is a product, which, as regards suitability for toilet purposes, has a distinct advantage over ordinary curd soaps. A certain quantity of glycerine in a soap renders it easily soluble in water and hereby causes a good lather, and, furthermore, imparts to the soap a nice transparent appearance.

As is already known, glycerine soaps can now be obtained quite cheaply, they are quite transparent, and look almost like yellow glass, and also have the quality of making a good lather.

Before glycerine was applied in soap-making, transparent soaps could only be obtained by dissolving perfectly dry soaps in alcohol, and the alcohol was then distilled from the soap. These soaps were certainly very transparent, but on account of the small percentage of water contained, were only dissolved with difficulty and, therefore, hardly suitable for toilet purposes, and moreover—owing to the troublesome preparation—could only be obtained at fairly high prices.

Now hardly any transparent soaps are made in this manner, but for this purpose glycerine is exclusively used, which also possesses the advantage that by dissolving the colouring matter in the glycerine it imparts nice colours to the transparent soap.

If to heated glycerine, which has been diluted with about one third of its volume of water, as much finely cut soap is added as can be dissolved therein, without the mass on cooling becoming hard, a product is the result which in the trade is known under the name of "Liquid Glycerine Soap" or "Glycerine Cream" and, coloured and scented in various manners, forms a very valuable toilet adjunct.

If in the process of soap making pure glycerine is replaced by a glycerine which contains different medicinal substances in solution, then in this manner soaps can be obtained which can be designated as cosmetic-medicinal soaps as they beautify the skin and also act medicinally.

The solvent action of glycerine on scents and colouring matters can be made use of by dissolving these substances in suitable quantities in the glycerine, and merely combining this solution with soap. In order, however, to obtain the better quality glycerine soaps, there is a special process, and this is carried out either by adding and stirring the appropriate quantity of glycerine and sugar solution into the soap after it has been boiled and then letting it cool in moulds, or by melting ready-made soap and adding glycerine, or, finally, by preparing a solution of soap in alcohol, mixing this with glycerine, and then distilling off alcohol.

According to the first process, soaps of alabaster-like appearance can be obtained; if the second method is resorted to, soaps are made the transparency of which is similar to that of a dimmed glass; with the latter, however, and the exercise of care, such soaps can be made which are perfectly transparent, and if no colouring matter is added they have the appearance of yellow glass.

It is unfortunately impossible to discuss in detail in this work, which is dedicated to the application and properties of glycerine, the very extensive and important application of glycerine to toilet soap manufacture. Those who are interested in this subject and would like further details should read the work on "Soaps" by G. H. Hurst, published by Scott, Greenwood & Son, London. Here we can only give a few indications as to the production of glycerine soaps.

If it is intended to make glycerine soaps by direct saponification—crutching—then the filling substances, glycerine and sugar, should be added to the soap mass immediately after saponification.

The production of soap by direct stirring with glycerine has been modified, in such a manner that a soap is obtained which is filled, coloured, and scented and further has a very high degree of transparency. The process used is the following:—

Refined tallow	80 kg.
Coconut oil	40 ,,
Hog's lard	80 ,,
Soda lye 40° Bé	90 ,,
Potash lye 40° Bé	10 ,,
Glycerine 28° Bé	20 ,,

The boiler in which the production of the soap takes places is generally a fairly shallow one and provided with a stirring device. Above the pan there is a cask containing the lye; through a glass pipe which by means of a rubber tube is fastened to the cock of the cask, the lye can gradually be admitted to the contents of the pan. The glycerine is in a lead vessel which stands rather high and which also must be supplied with a cock and glass pipe.

For the production of fine coloured and highly transparent soaps, it is absolutely necessary to use very pure raw materials; in the case under discussion it is strongly recommended to use the lye obtained by means of lime, not that prepared from wood ashes but that from potash, as lye obtained from wood ashes is generally of a fairly dark colour. Skill is needed in dissolving the potash; generally one and a half times its weight in water is poured over it, and for this purpose very cold water is used. In this the potassium carbonate only is principally dissolved, as the foreign salts remain undissolved. The solution is separated from the deposit, diluted sufficiently with water, and rendered caustic with lime.

Before proceeding to the real saponification the mixed lyes are placed in the cask and the glycerine in its receiver. The colouring matters to be used are at once dissolved in the glycerine (for the case in question soluble colouring matter must be used, as by using non-soluble colouring matter the soaps will not be transparent), and to the glycerine is added the aromatic substance for scenting the soap.

In order that the mixture of the solution of colouring matter and aromatic substances with the glycerine should be thorough, part of the glycerine is placed in a china bowl, heated up to about 60-80° C. and the colouring matter (fuchsine red, methyl violet, iodide green, etc.) in solid form is added; by stirring with a pestle it is spread through the liquid, and solution follows in a very short time. After the glycerine has cooled again, the aromatic substances are added, and the liquid poured into the glycerine receiver. The dish is rinsed out with glycerine and the solution in the glycerine receiver is stirred with a glass rod and mixed with the remaining glycerine.

Then so much lye is placed in the pan that it stands about a hand high, and it is heated to about 100° C., when the fat is added, and by the movement of the stirring device it melts on the hot liquid. When all the fat is melted, all the lye is poured in in a thin stream and constantly stirred, and this heating and stirring are continued for so long until the soap shows the requisite quality. If too thick, owing to strong evaporation of the water, this can be remedied by adding and stirring in the necessary quantity of hot water.

The soap still under the process of stirring is allowed to cool as much as possible without it thickening, and then the glycerine, that is the solution of colouring matter and perfume in glycerine, is slowly poured in and mixed with the soap by constant stirring. The whole work is easy of accomplishment, if care is taken that the stirring apparatus moves easily and is in good working order, as otherwise constant stirring is certainly a very tiring process.

The soap, now finished, is placed in cake moulds and in these left to cool slowly. The longer the cooling takes place the more transparent will the soap be; as these soaps contain dissolved substances only, there is no reason to fear separation of the colouring matter, and the finished cake of soap has an even appearance.

If glycerine soap is to be made by remelting, first of all water is placed in the pan, this is heated, the pieces of soap are added, mixed by stirring with the water, and as regards the addition of glycerine, colouring, and aromatic substances, the same process is followed as above described.

PRODUCTION OF TRANSPARENT GLYCERINE SOAPS.

Ordinary soaps are not transparent, or only faintly so, as the sodium salts of the fatty acids are present in a crystallized state, and the crystals reflect the light in different directions. Snow which consists of colourless ice crystals appears white and non-transparent as the surfaces of the crystals reflect the light in all directions. Just the same thing occurs with soap crystals.

Snow sodden in water is very transparent because the water in the spaces between the crystals alter the light refracting conditions. If to a soap light refracting glycerine is added, something similar takes place as when soaking snow in water, and the result is that glycerine soaps have a very transparent appearance.

Perfectly transparent glass-like soap can only be obtained if the soap is not crystallized but amorphous, and this can only be obtained by adding to the soap methylated spirits, glycerine, and sugar.

As soaps made in this manner are very hard and also require a long time to dissolve in water and make a lather, it is advisable from the outset to use a softer soap. If, however, transparent soaps are filled with glycerine as is now almost always the case, and large quantities of glycerine used, then this circumstance is less significant, as glycerine already makes the soap softer and, being itself a substance easily dissolved in water, increases the solubility of the soap.

The soap is cut into shavings by a planing machine; in this case, however, it is necessary to use a mill which gives very fine shavings, not thicker than a sheet of writing paper. These shavings are spread out in thin layers on linen stretched out on a frame and then thoroughly dried in a drying room. The drying process must continue until the shavings crumble to dust on being pressed between the fingers, which can be taken as a proof that the soap is absolutely free from water.

The dry shavings are then taken from the drying-room and placed in the retort of a distilling apparatus, the head of the latter is fixed on and 90 per cent alcohol poured into the retort. The stirring device of the distilling apparatus is set in motion, and the contents of the retort slowly heated until it boils, when the soap is dissolved in the alcohol into a paste-like mass The evaporating alcohol is condensed in the cooling coil of the distilling apparatus and caught in a bottle placed before the opening of the coil.

As soon as it is certain that all the soap has been dissolved, the glycerine mixed with the colouring matter and perfume is introduced into the retort through a tube fitted into the head, and mixed with the soap paste by constant stirring. The heating is continued until all the alcohol used for dissolving the soap is distilled off, the soap is then run into moulds in which it rapidly solidifies.[1]

If the operation is carried out in the proper manner (the essential point is that the soap should be free from water and absolutely dissolved in the alcohol) it is perfectly transparent in the moulds.

According to the modern and now universally adopted practice, the saponification is accomplished solely with soda lye, the fatty ingredients consist mostly of tallow, coconut, and castor oil, and occasionally, in order to obtain hard soaps, stearine is also added. It is advisable to filter the melted fats in order to remove any impurities. The 40 per cent soda lye necessary for the saponification is then mixed with half the quantity of methylated spirits, and added to the melted fat in the pan at a temperature of about 60°. In order to prevent as far as possible evaporation of the alcohol, the pan should have a cover that fits very well.

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[1] (*Translator's Note.*—It is impossible to distil off all the alcohol from the soap.)

Saponification then follows very rapidly, and when all the fat is saponified the solution of sugar and glycerine in distilled water, to which half the amount of methylated spirits has been added, is well stirred in. The temperature of the contents of the pan is then raised to about 85° and kept at this for an hour and the pan must remain covered. If a sample of the soap is then poured on to a glass plate and left to solidify, it should be transparent (not dull and dirty) and firm.

The soap is then let cool to 70° and at this temperature coloured. When the temperature has sunk to 68° the perfume, dissolved in the remainder of the alcohol, is added.

If the perfume contains large quantities of oil, then to a batch of soap as much 20° potash lye must be added again as is equal to the weight of the oil containing aromatic substances; unsaponified oil would dim the transparency of the soap. Transparent, excellent soaps can be obtained according to Deite as follows:—

	I.	II.
Tallow	50 kg.	45 kg.
Cochin-Coconut oil	45 ,,	40 ,,
Castor oil	15 ,,	25 ,,
Soda lye 40° Bé.	50 ,,	50 ,,
Methylated spirits 90 per cent	35 ,,	30 ,,
Sugar	20 ,,	25 ,,
Distilled water	20 ,,	20 ,,
Glycerine 28° Bé	25 ,,	22 ,,

For colouring only pale yellow (lemon or wax yellow) colouring substances are used. For scenting the following are used:—

Geranium oil	240 g.
Verbena oil	200 ,,
Palma Rosa oil	160 ,,
Bergamot oil	170 ,,
Bitter almond oil	10 ,,
Tincture of musk	20 ,,

Geranium oil	240 g.
Oil of lavender	160 ,,
Oil of cinnamon	140 ,,
Caraway oil	120 ,,
Clove oil	100 ,,
Tincture of musk	20 ,,

PRODUCTION OF LIQUID GLYCERINE SOAPS.

Liquid glycerine soap of the consistency of syrup is at present a much sought after toilet adjunct, and is mostly coloured with pale brown (honey glycerine soap) or with pale pink and perfumed with geranium oil (rose glycerine soap) and supplied to the trade.

Particularly fine specialities in glycerine soaps are mignonette glycerine soap (perfumed with mignonette oil and coloured pale green) and lavender glycerine soap (scented with lavender and coloured pale blue).

As regards its constitution glycerine soap is a potash soap, dissolved with or without addition of alcohol in very little water and mixed with scented and coloured glycerine. It is produced by saponification of pure olive oil with potash lye, and dissolving 100 parts of this soap in a mixture composed of 50 parts of water and 50 parts of alcohol at 40 per cent and adding 10 parts of glycerine. This soap solution is a yellow brown and a certain amount of colouring matter need only be added in order to obtain the honey-coloured article.

Pure potash oleine soap is an excellent material for the manufacture of liquid glycerine soaps, and these can be made without using alcohol. Oleine or oleic acid (from stearine works) is placed in glass bottles and stored for several months in a cool place the temperature of which can sink to 0°. During this time, the greater part of the stearic and palmitic acid dissolved in the oleine sinks to the bottom of the bottle in a crystalline mass and the liquid above it appears quite clear. It is carefully poured off from the deposit, filtered through thick linen, in order to retain all foreign substances which may be floating about in it, saponified in the cold with caustic lye made from potash, and the total amount of the glycerine, with the exception of a very small quantity, is added, This remainder of glycerine is used in order to dissolve in it the colouring and aromatic substances, and is only added when the soap has cooled. If the cooled soap should be too thick, then this drawback can be remedied by the addition of a fairly concentrated pearlash solution (not caustic) The ordinary proportion of the glycerine addition to this soap is 3 parts of glycerine to 1 part of oleine, to be saponified.

GLYCERINE COLD CREAM SOAP.

The following directions are given for the production of glycerine cold cream soap:—

30 kg. of coconut oil, 20 kg. tallow, 8 kg. of castor oil, 2 kg. of crude palm oil are heated together at 75° C.; 30 kg. of caustic soda lye at 36 per cent are added and stirred, 2 kg. of glycerine and ½ kg. of spermaceti, this latter having previously been warmed to 75° C., are added and stirred in.

Then the soap is covered up and left to heat spontaneously, which will have taken place in about one hour and a half. A clear yellow, firm soap is the result which is very similar to a settled soap.

The soap is now placed in the mould and perfumed with 50 g. cassia oil, 50 g. bergamot oil, 100 g. lavender oil, 60 g. of tincture of musk, 80 g. tincture of benzoin, 20 g. wintergreen oil, 30 g. clove oil, and 10 g. cinnamon oil.

GLYCERINE APPLIED IN MEDICINE.

Owing to its softening and dissolving properties glycerine is widely applied in medicine. It is used either as a solvent for certain substances, for instance for pepsine, or for the production of preparations with a softening action. Glycerine plaster of the German pharmacopœia is made, e.g., by warming 1 part of wheat starch with 10 parts of glycerine in a water-bath for so long until the starch has formed into a paste, and consists therefore of a paste mixed with glycerine. The great dissolving properties glycerine possesses for many chemical preparations enables the incorporation in this paste of a large number of medicinal preparations, and in this manner renders it possible to produce medicaments which must be of very powerful efficacy, as glycerine is easily absorbed by the skin.

Many preparations which are used for cracked skin, redness, also as remedies for chilblains, contain glycerine, and owe the greater part of their efficacy to the glycerine contents.

Liquid soaps for medicinal purposes can be made according to the following prescriptions:—

LIQUID TAR SOAPS.

Two hundred parts of tar are mixed with 400 parts of oleic acid, slightly warmed and filtered. The water contents has no detrimental action in this case. This is warmed in a water-bath, stirred and neutralized with a little alcoholic potash solution. To the soap formed, 100 parts of alcohol are added, and further, some olive oil in order to prevent irritation by any excess of potash, and made up with glycerine to 1000 parts. This 20 per cent tar soap is said to comply with the highest claims. Mixed with two parts of distilled water, the soap leaves no deposit on the sides of the vessel.

LIQUID STORAX SOAPS.

The process is the same as that in the case of the soap just discussed. The digestion with oleic acid enables raw storax balsam to be used, from which the grosser impurities are removed by filtration. The finished soap settles out; it must therefore be well shaken, and should be stored in dark-coloured glass vessels.

SUPERFATTED LIQUID LANOLINE GLYCERINE SOAPS.

A soap recommended as an excellent toilet adjunct can be made as follows: About 10 per cent lanoline is dissolved in oleine, saponified as in the case of the tar soap and scented, and most suitable for this purpose is a solution of coumarin in geranium oil. Further, to the finished soap, tincture of benzoin can be added.

A soap intentionally made alkaline, corresponding to the ordinary glycerine soaps, is particularly suitable for disinfection purposes, and for this reason should realize a good sale.

LIQUID ANTISEPTIC SOAPS of best possible neutrality can, according to Antoine, be obtained as follows:—

Caustic potash at 70 per cent, as free as possible from carbonate . .	50 g.
Sweet almond oil	200 ,,
Glycerine (30° Bé)	100 ,,
Distilled water	1000 ,,

The potash is dissolved in twice its weight of water, and the oil and glycerine added and stirred round. The remainder of the water is then added and the mixture is kept in a water-bath twenty-four to thirty-six hours at 60°-70° C. The non-saponified oil is taken off and a jelly-like mass is obtained of which 900 g. are mixed with 70 g. of alcohol at 90 per cent, and 10 g. each lemon, bergamot, and verbena oil. This is warmed for a few hours at 60° C., cooled, and the separated potassium stearate filtered through cotton wool. The filtrate then remains clear. It contains 0·8 to 1 g. of free alkali in the kilogram. This can be neutralized by introducing a stream of carbonic acid or by the addition of a glycerine solution of tartaric acid.

GLYCERINE AS ADDITION TO WINE, BEER, AND LIQUEURS.

In the spirituous fermentation of wine-must, beer-wort, brandy mashes, etc., in a word, in every case in which alcohol is formed by a fermentation process, glycerine also is formed; the following may be taken as general products of fermentation—alcohol, carbonic acid, and glycerine.

The quantities of glycerine resulting from fermentation vary considerably, and in wine amount to between 0·2 and 2·0 per cent, whereas in beer, brewed according to German methods, there is, on an average, 0·6 per cent of glycerine.

It has been found that the glycerine contents of wine has much to do with its flavour, and that in addition to the sweet taste possessed in a high degree by glycerine, it also imparts to it those qualities which are designated as maturation and oiliness.

This maturation cannot be explained in words, it must be recognized by practical experiments. The quality of the oiliness of the wine consists therein that when wine is swung round in a glass on flowing down it leaves on the sides of the glass oily streaks, this is generally looked upon as a good quality of the wine and highly esteemed by consumers.

In addition to the qualities mentioned, glycerine possesses that of masking the rough sour taste peculiar to wines containing much acid, and hereby renders the taste of the wines in question much more pleasant.

Since it has been possible to obtain commercial glycerine of such a high degree of purity, extensive application has been made of it to the wine trade, and to some wines certain quantities of glycerine have been added in order to render the taste milder, more mature, and at the same time make the wine more oily; this addition has been designated as Scheelerizing or glycerinizing wines.

We would, however, lay particular stress on the fact that the modern law in connection with foodstuffs has *condemned* and *prohibited* the adulteration of beverages with glycerine. When we make mention of the subject in this connection, we only do so to draw attention to this fact and to the distinct warning not to add glycerine to beverages intended for sale. And it would not be wise for anyone to attempt to do this in the hope that the slight addition of glycerine will not be detected. The chemistry of foodstuffs has nowadays made such rapid strides that this would be no difficult task at all, although, as we have already mentioned, glycerine is a normal product of alcoholic fermentation. However, the individual component parts of a natural wine, etc., exist in the wine in certain proportions which vary but little. This would at once be a help in detecting the addition of glycerine, alcohol, sugar, etc., that is of absolutely normal ingredients of wine, as thereby the normal proportion of the substances would be altered.

The quantity of glycerine to be added to a hectolitre of wine is best ascertained by first adding 50 g., equal to a thousandth part of the weight of the wine, mixing it thoroughly, and tasting a sample. If this proves insufficient, then further amounts of 10 g. of glycerine are added, until the wine as regards maturation and oiliness has acquired the requisite quality.

It must be remarked in this connection that wine treated in this manner should not be used at onc as at the beginning an experienced tongue would at once recognize this addition of glycerine, and it takes some time before the taste of the glycerine and that of the wine have combined harmoniously. In order to attain this, it is necessary that the wine should be stored for several weeks, and after this period even a good wine connoisseur would not be able to recognize that glycerine had been intentionally added to the wine, presuming, of course, that this adulteration does not go beyond a certain degree.

It has also been found preferable to proportion the glycerine addition according to the quantity of free acids contained in the wine, and to increase the glycerine in proportion to the increasing acidity of the wine. The following short table gives this proportion:—

Acid contents in thousandths	Glycerine, grammes per hectolitre
7·0	00
7·5	80
8·0	160
8·5	240
9·0	320
9·5	400
10·0	480
10·5	560
11·0	640
11·5	720
12·0	800

Although these tables are quite suitable for certain cases, yet the addition of glycerine in such small quantities as 10 g. and repeated taking of samples is preferable, as one must endeavour to avoid any excess of glycerine as thereby the taste of the wine would be altered in a striking manner and the addition easily detected. It must, however, be considered as a rule strictly to be observed, never to add such large quantities that they strike the sense of taste unpleasantly.

In addition to the influence which glycerine has on the taste of wine, it also exercises an influence on the behaviour of the wine. Wines which have fermented for some time, and accordingly can only be clarified very slowly, soon settle if glycerine is added and they clarify rapidly. This phenomenon can be explained by the fact that the glycerine, although itself a product of fermentation, opposes spirituous fermentation; the faint after-fermentation which still takes place in the wine can then be completely suppressed by the addition of the requisite quantity of glycerine.

Glycerine added to beer has the same action on its qualities as in the case of wines; the beer is matured, sweeter in taste, and also retains the froth longer, after it has been poured into a glass. As beer, however, contains far less glycerine than wine, on no account should such large quantities of glycerine be added to the beer as to the wine, and an addition of 250 g.-300 g. per hectolitre should be the highest measure in which it can be applied.

The right moment for adding glycerine to beer depends upon what is to be done with the beer. If it is intended to leave it for a long time in storage casks, then it is to the interest of the brewer to modify the intensity of the fermentation very considerably, so that on prolonged storage the beer shall not ferment to such a degree that it becomes "winey," and this could be accomplished by storing the beer in very cold cellars. Such beers should be doctored with glycerine immediately after they are placed in the storage cask, because in this case glycerine assists in moderating the fermentation process.

In the case of beers which are only to be stored for a short time, the glycerine is best added about fourteen days before the beer is ready to be broached. The glycerine should be dissolved in the beer, poured into the storage cask, and this should be firmly bunged up. The glycerine thus has the time to distribute itself evenly through the whole mass of the beer, and by bunging, the beer is thoroughly supplied with carbonic acid until it is wanted for running off.

Glycerine has also been applied to the manufacture of liqueurs, and it is recommended as addition in place of sugar. Such an addition has decided advantages, because the glycerine imparts its pleasant sweet taste to the liqueurs, and, moreover, contributes to the liqueurs that oily characteristic which is so much esteemed in so-called oils or creams, the choicest and most expensive liqueurs.

Glycerine also possesses the quality of dissolving essential oils and thereby assists the dissolving action of alcohol, so that by adding glycerine to a liqueur substance, a great many more essential oils are brought into solution than would be possible by the action of the alcoholic contents alone

In connection with the application of glycerine to the manufacture of liqueurs, there is one precaution to be observed, that is, that the quantity of glycerine added to the liqueur should not exceed a certain measure. The reason for this is the fact that one cannot enjoy a liqueur which contains a large amount of glycerine, whereas it is to the interests of manufacturers to make the liqueurs in such a manner that a great deal of them are sold.

We would again call attention to the prohibition of the application of glycerine; this refers also to the manufacture of liqueurs.

Glycerine for Filling Gas Meters.

Gas meters, as is known, are filled with water, but this method has certain drawbacks, the greatest of which is that water is being continually carried away through the gas, and therefore repeated filling with water is necessary. In order to remedy this drawback, in many places glycerine has been substituted as filling for gas meters and with good results.

Owing to its hygroscopic qualities glycerine not only gives out no water, but absorbs water from the gas; as a rule glycerine diluted with 15 per cent water, absorbs from the gas in the course of the year 12-15 per cent of water, and then it can also happen that on cold days the glycerine in the gas meter may freeze and the working be interrupted for some days.

The glycerine contained in the gas meter not only absorbs water from the gas, but also absorbs certain other combinations, in particular sulphide ammonium and sulphite, and from time to time (about once a year) must be taken out of the gas meter and cleaned.

The cleaning process is most simply accomplished by heating it for some hours up to 130° C. in a covered boiler connected with a flue which draws well, whereby the greater part of the substances dissolved in the glycerine can escape. The tar-like substances which are absorbed from the gas remain in the glycerine. As soon as a sample of the glycerine does not show an alkaline reaction on cooling the heating is stopped, and the glycerine is decolorized by filtration over bone charcoal, when it can again be used for filling the gas meter.

The advantages offered by filling gas meters with glycerine consist therein that repeated filling is avoided, and, moreover, the gas is cleaned by glycerine, and a glycerine filled gas meter freezes much more seldom than a water filled gas meter.

Owing to its indifference to metals, glycerine is eminently adapted to protect metals which rust easily, such as polished iron or steel. To this end, it is only necessary to thoroughly rub the metal objects with a cotton wool pad which has been dipped in glycerine and then pressed out, and the thin layer of glycerine which is spread on the metal prevents rusting for some time.

Glycerine has also been used as a lubricant for the component parts of delicate machinery, for instance of watches; it would moreover, owing to its indifference to metals, be most suitable for this purpose if it did not possess the quality of drawing humidity from the air. Glycerine, however, diluted to a certain degree with water, loses its thick oily consistency, and is no longer suitable to prevent friction between the parts of machinery.

GLYCERINE FOR CLAY MODELLING.

Sculptors, as is well known, make use of a soft clay mass for their first rough modelling, and on ceasing to work cover it with damp cloths in order to prevent drying of the clay. In the production of large, plastic works, this is accompanied with some difficulty, for the clay models not only crack on drying, but the shape of the model also changes owing to the shrinkage of volume which takes place as the clay drys.

These drawbacks can easily be remedied by preparing the clay not with water but with a liquid composed of 3 parts of water and 1 part of glycerine; the water-attracting quality of the glycerine prevents entire drying of the clay, without it being necessary to take any other precautions in regard to this drying, and for this purpose an inferior glycerine of a dark colour can be used.

GLYCERINE APPLIED TO THE WEAVING INDUSTRY.

Glycerine can be very extensively applied to the textile industry and particularly to the manufacture of the most delicate cotton fabrics (muslin weaving) and also to the manufacture of fine laces. In order to impart to the cotton threads which are used in the manufacture of this fabric the necessary degree of suppleness they must continually be kept damp, and formerly such textures were mostly manufactured in damp cellar rooms. Naturally the continual sojourn in such rooms was injurious to the health of the workers. Therefore the threads were impregnated with a dressing which kept them continually damp.

Preferably mixtures of dextrin and grape sugar solutions were used on account of their water-attracting property, but they were not very suitable; only since glycerine has been added to these dressing compositions have the results been satisfactory, and the most delicate muslin fabrics and lace work can now be manufactured in perfectly dry and airy rooms.

The compositions which are used for these dressings are very numerous and consist mostly of dextrin, aluminium sulphate, and glycerine, for instance:—

Dextrin	5 parts
Aluminium sulphate . . .	1 „
Dissolved in water . . .	30 „
Mixed with glycerine	12-15 „

The dressing remains continually damp, has no smell, and is not liable to become mouldy.

Glycerine can be used with great advantage in different branches of the textile industry, in all cases where it is a question of imparting to the cotton or fabric suppleness and softness, and the simplest form of application consists in adding it to the water with which the cotton yarn or fabric are to be washed: on drying the fabrics the glycerine remains dispersed throughout the whole mass of the fibre, and gives it such a high degree of suppleness and elasticity that the value of the fabric in question is thereby considerably increased.

GLYCERINE APPLIED TO THE MANUFACTURE OF PAPER, TOBACCO, ETC.

Paper which is made from straw and wood substance only, or with the addition of these materials, often possesses the undesirable quality of brittleness and hardness, and often on merely folding breaks. The quality of paper also in respect to suppleness can be considerably improved if to the paper pulp, consisting of paper substance and water, a small percentage of glycerine is added; it prevents entire drying of the finished paper and also the resulting brittleness.

Glycerine is also made fairly considerable use of in the manufacture of tobacco, and in the preparation of snuff and chewing tobacco, which, when glycerine is added, does not dry up.

Wood which has been impregnated with glycerine obtains a high degree of suppleness, and even brittle wood, impregnated with glycerine, can easily be bent without cracking, a fact which should be of great consideration to the wood-worker. In order to render wood more receptive for glycerine, it is as well to dry it thoroughly in a kiln, and while it has a temperature of 70°-80° either to place it in glycerine or to coat it with it. Glycerine is eagerly absorbed by the hot wood and penetrates very deeply. Casks, made of wood which is impregnated with glycerine, can remain some time exposed to the air without becoming non-waterproof, because glycerine being a water attracting substance keeps the wood continually damp. Also, such casks do not assume any musty or unpleasant smell inside as glycerine arrests the development of the small fungi which cause this smell.

CHAPTER XV.

CHEMICAL ANALYSIS OF GLYCERINE.

SINCE glycerine has attained such importance for many industries and particularly since it has been used in such large quantities for explosive preparations, the analytical determination of glycerine in a liquid has become of considerable value, and several methods are used in order to determine the amount of pure glycerine contained in a given substance.

In commerce different sorts of glycerine are distinguished, according to method of production, whether distilled or not, as also to purity and concentration. According to their origin crude glycerines can be divided into *saponification glycerine* from autoclave saponification, or fat-splitting, according to the Twitchel method, *distillation glycerine,* which is a by-product obtained by the saponification of fat with acid and cleaned by distillation, and soap-lye glycerine obtained from spent lyes from soap-boiling.

The most impure glycerine is the lye glycerine, obtained from the spent lye in soap manufacture. Its ash content amounts mostly to 10 per cent and is due to the presence of common salt, soda, caustic soda, and also sodium sulphate. Further, lye glycerine often contains gelatinous and resinous substances, and carburet of hydrogen. It is light brown to brown red in colour, the specific gravity is 1·3 or 34° Bé, and the glycerine content 80-82 per cent. The high content of ash, the strong chlorine reaction, and the high specific gravity are all points by which it can be recognized.

Distillation glycerine possesses a sharp astringent taste and smell. The percentage of ash is 3·5 per cent; further, organic impurities are always present. The concentration is usually 28 Bé, the glycerine-content between 84 and 86 per cent. The colour is straw yellow to dark amber, and distillation glycerine can be recognized inasmuch as lead acetate gives a strong deposit, and on hydrochloric acid being added it becomes very muddy, due to the liberated free fatty acids.

Comparatively, the purest is the saponification glycerine. It contains only 0·5 per cent ash, but much lime and magnesia. It is also concentrated to 28° Bé and differs from distillation glycerine in that when treated with lead acetate there is only a slight and slow deposit, and hydrochloric acid does not cause any turbidity.

The purest is the double distilled glycerine with a percentage of water of only 2-3 per cent. It must be colourless and should not possess any unpleasant smell. Once-distilled glycerine must also answer these requirements, but it generally contains slight quantities of salts.

For the purposes of soap manufacture glycerine free from lime should be used; it does not need to be distilled, but should be free from lime compounds.

Glycerine to be used for the manufacture of nitroglycerine, that is in the manufacture of dynamite, is mostly once-distilled, but concentrated glycerine should only contain small quantities of impurities. On the other hand, the colour is a matter of secondary importance, provided it is not due to large quantities of impurities. The specific gravity should not be less than 1·261 at 15·5° C.

Refined or commercial glycerine is mostly not quite odourless and contains different impurities, particularly dissolved salts; it is usually met with at concentrations of 18-24 and 28° Bé.

Double distilled chemically pure glycerine should, according to the indications in the German pharmacopœia, stand the following tests:—

A mixture composed of 1 c.cm. glycerine and 3 c.cm. zinc chloride solution should not during an hour assume a darker colour.

If glycerine is diluted with 5 parts water and mixed with sulphuretted hydrogen water, barium nitrate, ammonium oxalate, or a solution of calcium chloride, there should be no precipitate or cloudiness. Silver solution should only cause faint opalescence.

Five grm. heated in an open dish and ignited, burns away leaving a dark stain which on being heated still further completely disappears.

If a mixture of 1 grm. of glycerine and 1 c.cm. of ammonia liquid is heated in a water-bath to 60° and then at once mixed with three drops of silver nitrate solution, then within five minutes there should be neither coloration nor a brown black deposit in this mixture.

Two c.cm. of glycerine warmed with 1 c.cm. of soda lye, should give no coloration, neither should there be any ammonia or smell of glue-like substances evolved.

One c.cm. of glycerine gently warmed with 1 c.cm. of diluted sulphuric acid, should give no unpleasant rancid smell.

DETERMINATION OF GLYCERINE CONTENTS.

If pure glycerine is being dealt with, the water contents can be easily ascertained by the specific gravity by means of the tables given below. But particular attention must be paid to the temperature as these tables only give correct values at those temperatures for which they have been calculated.

As is well known, the specific gravity of the liquid is influenced by temperature in such a way that a certain rise of temperature gives the liquid a lower specific gravity.

This method is only applicable when absolutely pure glycerine is being considered, that is such that does not contain any appreciable quantities of impurities. If this is not the case, particularly with glycerine in admixture with numerous other substances, for instance, soap-lye glycerine, then another process must be resorted to in order to determine its quantity, which is based on the oxidation of glycerine. In this case mostly the methods of Legler and Hehner are

TABLE FOR THE DETERMINATION OF THE WATER CONTENTS OF GLYCERINE ACCORDING TO CHAMPION AND PELLET AT 17·5° C.

Water in 100 pts. Glycerine.	Specific Gravity.	Degree According to Beaume Aerometer.	Water in 100 pts. Glycerine.	Specific Gravity.	Degree According to Beaume Aerometer
0·0	1·2640	31·2	11·0	1·2350	28·6
0·5	1·2625	31·0	11·5	1·2335	28·4
1·0	1·2612	30·9	12·0	1·2322	28·3
1·5	1·2600	30·8	12·5	1·2307	28·2
2·0	1·2585	30·7	13·0	1·2295	28·0
2·5	1·2575	30·6	13·5	1·2280	27·8
3·0	1·2560	30·4	14·0	1·2270	27·7
3·5	1·2540	30·3	14·5	1·2255	27·6
4·0	1·2532	30·2	15·0	1·2242	27·4
4·5	1·2520	30·1	15·5	1·2230	27·3
5·0	1·2505	30·0	16·0	1·2217	27·2
5·5	1·2490	29·9	16·5	1·2202	27·0
6·0	1·2480	29·8	17·0	1·2190	26·9
6·5	1·2465	29·7	17·5	1·2177	26·8
7·0	1·2455	29·6	18·0	1·2165	26·7
7·5	1·2440	29·5	18·5	1·2150	26·5
8·0	1·2427	29·3	19·0	1·2137	26·4
8·5	1·2412	29·2	19·5	1·2125	26·3
9·0	1·2400	29·0	20·0	1·2112	26·2
9·5	1·2390	28·9	20·5	1·2100	26·0
10·0	1·2375	28·8	21·0	1·2085	25·9
10·5	1·2362	28·7			

used, whereby glycerine in the presence of sulphuric acid is by means of bichromate oxidized to carbonic acid, when the amount of the oxidizing substance used up is determined with ferrous ammonium sulphate. If according to this method correct results are to be obtained, then the liquid to be analysed should be free from chlorine and as far as possible from organic substances. According to the regulations of the Analytical Committee of the Convention of

TABLE OF THE SPECIFIC GRAVITIES OF MIXTURES OF GLYCERINE WITH WATER (ACCORDING TO W. LENZ). FOR TEMPERATURES OF 12°-14°.

Contents of the liquid in anhydrous glycerine, in per cent	Specific Gravity of the liquid	Contents of the liquid in anhydrous glycerine, in per cent.	Specific Gravity of the liquid	Contents of the liquid in anhydrous glycerine, in per cent	Specific Gravity of the liquid
100	1·2691	66	1·1764	32	1·0825
99	1·2664	65	1·1733	31	1·0790
98	1·2637	64	1·1702	30	1·0771
97	1·2510	63	1 1671	29	1 0744
96	1·2584	62	1·1640	28	1·0716
95	1·2557	61	1·1610	27	1·0689
94	1·2531	60	1·1582	26	1·0663
93	1·2504	59	1·1556	25	1·0635
92	1·2478	58	1·1530	24	1·0608
91	1·2451	57	1·1505	23	1·0580
90	1·2425	56	1·1480	22	1·0553
89	1·2398	55	1·1455	21	1·0525
88	1·2372	54	1·1430	20	1·0498
87	1·2345	53	1·1403	19	1·0471
86	1·2318	52	1·1375	18	1 0446
85	1·2292	51	1·1348	17	1·0422
84	1·2265	50	1·1320	16	1·0398
83	1·2238	49	1·1293	15	1·0374
82	1·2212	48	1·1265	14	1·0349
81	1·2185	47	1·1238	13	1·0332
80	1·2159	46	1·1210	12	1·0297
79	1·2122	45	1·1183	11	1·0271
78	1·2106	44	1·1155	10	1·0245
77	1·2079	43	1·1127	9	1·0221
76	1·2042	42	1·1100	8	1·0196
75	1·2016	41	1·1072	7	1·0172
74	1·1999	40	1·1045	6	1·1470
73	1·1973	39	1·1017	5	1·0123
72	1·1945	38	1·0989	4	1·0097
71	1·1918	37	1·0962	3	1·0074
70	1·1889	36	1·0934	2	1·0049
69	1·1858	35	1·0907	1	1·0025
68	1·1826	34	1·0880		
67	1·1795	33	1·0852		

German glycerine manufacturers, the following is carried out:—

The following aqueous solutions are to be made and used at 15° C.:—

(*a*) Potassium bichromate solution, which in a litre contains exactly 74·86 grm. of potassium bichromate and 150 cm.^{3} of concentrated sulphuric acid. One cm.^{3} of this solution is equivalent to 0·01 grm. of glycerine.

(*b*) Diluted bichromate solution. Obtained by dilution of 100 c.cm. of the solution (*a*) to 1000.

(*c*) Ferrous ammonium sulphate solution. Contains in a litre 240 grm. of ferrous ammonium sulphate and 100 cm.^{3} of concentrated sulphuric acid.

(*d*) Solution of red prussiate of potash 1 : 1000. This solution is always freshly prepared.

For the standardization of the ferrous ammonium sulphate solution, 10 cm.^{3} of the solution are titrated with the diluted bichromate solution, until a drop of the mixture with a drop of the red prussiate solution mixed on a white porcelain plate shows no visible blue coloration. Ten c.cm. of this solution corresponds to about 40 c.cm. of the diluted bichromate solution, that is 4 c.cm. of the concentrated bichromate solution.

The determination of glycerine in spent lye with the help of these reagents is carried out in the following manner:—

About 20 grm. of spent lye which, however, must not contain more than 2 grm. pure glycerine are placed in a measuring flask of 200 c.cm. contents, carefully weighed and practically neutralized with diluted acetic acid with a specific gravity of 1·041, and the mixture must on no account be acid. Then this is diluted with distilled water to a volume of about 50 c.cm. and swirling round gradually, basic lead acetate solution, is added, until after standing for some time, the liquid, on the addition of a further drop of lead solution, does not show any further precipitate. It is then left for about half an hour and the mixture made up to 200 c.cm. at a temperature of 15° C.

Of this well-mixed and settled liquid, part is filtered through a dry filter. 20 c.cm. of this filtrate correspond to 2 grm. spent lye, and are now placed in an Erlenmeyer flask of 300 c.cm. capacity, when in the following order are added:

1. 30 c.cm. distilled water
2. 30 c.cm. diluted sulphuric acid
3. 25 c.cm. of concentrated bichromate solution.

This mixture is then suspended in boiling water for two hours and the flask covered with a small funnel.

After this time, and when the mixture has become cold, it is titrated back with the standardized ferrous ammonium sulphate solution until a drop of the mixture with the red prussiate of potash gives a blue coloration.

The calculation is then as follows:—

If, for instance, for the retitration of the oxidized liquid, that is the remaining excess of the bichromate solution, 40 c.cm. of the iron solution are used, then these correspond to 40 × 0·4 = 16 c.cm. of the bichromate solution. If these are now deducted from the 25 c.cm. added in the beginning, then 25 - 16 = 9 c.cm. of strong bichromate solution would be necessary for the oxidation of the glycerine, which corresponds to 9 × 0·01 = 0·09 glycerine. If this quantity was found in exactly 2 grm. spent lye, then this contains 0·09 × 50 = 4·5 per cent glycerine.

EXAMINATION OF GLYCERINE FOR DYNAMITE-MAKING.

For the examination of glycerine intended for dynamite- or nitro-glycerine manufacture, a nitration test is generally made, whereby is established how much nitro-glycerine can be produced from a given weight of glycerine. For this purpose, 15 grm. glycerine is nitrated in a glass cylinder with 70 c.cm. of a mixture of 37 per cent pure sulphuric acid, of specific gravity 1·5, and 63 per cent pure nitric acid of specific gravity 1·485 at a temperature not allowed to exceed 20° C. The nitro-glycerine should separate out from the acids with a sharp surface of separation, leaving no flocculent substances suspended in the under layer. Then the nitro-glycerine is separated from the acid in a separating funnel, washed with water at 35° to 40° C., then a few times with a 20 per cent soda solution, and finally again with water.

Theoretically 100 grm. glycerine should yield 246·7 grm. nitro-glycerine. But dynamite glycerine is never pure, and there is besides some loss in nitration, but the yield should be at least 207 to

210 per cent. In order to render nitro-glycerine harmless, it is best to run it into strong soda lye, whereby it is decomposed.

Under the title "Ein Beitrag zur Beurteilung des Dynamit-glycerins," Franz Hofwimmer, Vienna, publishes in the "Chemiker Zeitung," No. 5, 1912, the following:—

For glycerine intended for explosives manufacture a very high standard is fixed both as regards quality and concentration.

As is known, the nitration of glycerine is due to a reversible reaction; therefore it is striven, in order to secure the best possible yield, to reduce the mass of water present in the reaction to a minimum, which in the first place is accomplished by employing a water-free nitric acid, and an almost absolute glycerine. Further, the use of a glycerine containing much water would increase inadmissibly the danger of decomposition, or at least cause a very energetic development of heat. For this reason, dynamite glycerine must be at least 97·6 to 98 per cent, it should further evaporate at 180° C., leaving at the most 0·2 per cent residue, and only 0·05 per cent ash. It should contain neither reduction substances (acrolein) nor fatty acids, nor chlorine. The colour should be only wine-yellow, and the specific gravity at 15° C. should reach 1·2625 - 1·2630.

Although most dynamite glycerines answer these requirements, they notwithstanding often leave much to be desired on nitration as regards yield of nitro-glycerine, for which reason the usual methods of examination for this product give no definite results as to the yield of nitro-glycerine.

The frequently used method of Hehner yields indeed very exact results in the examination of crude glycerine; it is, however, more or less useless for determining the quality of dynamite glycerine. The method gives only correct results when the glycerine under examination is free from polyglycerols. These are formed during the distillation of glycerine as a consequence of local over-heating, and are able to affect very prejudicially the yield of nitro-glycerine. These polyglycerols result only from the splitting off of water, and in the estimation according to Hehner, all the C_3H_2 residue of the glycerine comes into consideration. Under these circumstances a glycerine examined by this method may show a $C_3H_8O_3$ content of more than 100 per cent. In nitro-glycerine manufacture, however, the quantity is only determined by the hydroxyl groups contained in the glycerine, so that a product containing polyglycerols yields a deficient quantity of nitro-glycerine. Whilst 92 grm. glycerine should yield theoretically 227 grm. nitro-glycerine, corresponding to 246·7 per cent, there results from the polyglycerols only the nitro-glycerine calculated from the formula $A = \frac{119x \quad 108}{92x}$ (where x is the number of compound $C_3H_8O_3$ molecules to a molecule). Diglycerine gives a theoretical yield of 188 per cent, and triglycerine only 168 per cent. To what extent a polyglycerol content is able to reduce the yield of nitro-glycerine is well illustrated by the following example. A dynamite glycerine that contained 86 per cent $C_3H_8O_3$, 10 per cent diglycerine, $C_6H_{14}O_5$, and 1 per cent water, gave according to the Hehner method of analysis, 97·08 per cent $C_3H_8O_3$, and 2·92 per cent of water, and should produce therefore on nitration a theoretical yield of 239·5 per cent nitro-glycerine; owing to the diglycerine content, however, the yield is reduced about 8·5 per cent, so that for the manufacture of nitro-glycerine the glycerine is not 97·08 per cent, but only 93·46 per cent. The nitrogen-content of nitro-glycerine obtained does not reach by far the theoretical figure of 18·50, so that the quality of the product is also unsatisfactory.

The examination of dynamite glycerine by the acetin method might be expected to give correct results, as will be understood from the foregoing, since it depends entirely on the quantitative estimation of the hydroxyl groups. It is, however, scarcely to be expected that the polyglycerols would be able to withstand a boiling of some hours with acetic anhydride, but on the contrary they hydrolyse to glycerine and are estimated as such. On this ground, the acetic anhydride method must also be rejected, apart from other defects of the process which must be taken into consideration.

Frequently it is attempted to determine the water contained in a glycerine by drying over sulphuric acid *in vacuo*. This method requires some considerable time and is, moreover, not quite accurate, since glycerine, on account of its energetic water-absorbing power, retains water under these conditions. All the remaining methods of glycerine estimation described in the literature leave much to be desired partly in accuracy, partly in simplicity.

The only accurate and absolutely reliable test for dynamite glycerine is therefore by nitration and determination of the nitro-glycerine produced. The well-known nitration apparatus of Novak and Schagel is not very suitable for a rapid and exact nitration, since in this only some 80-100 g. glycerine can be nitrated, a quantity which one can neither weigh accurately on the analytical balance nor with the ordinary scales. A nitration by means of the above-named apparatus, by the time that one has weighed the dried nitro-glycerine, takes at least 12-24 hours; working with proportionately larger quantities (150-200 g.) is a somewhat dangerous undertaking, especially for the inexperienced.

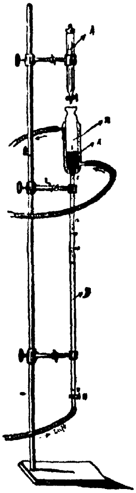

FIG. 7.

For the rapid, exact, and at the same time safe nitration, an apparatus has been devised, so constructed that it permits both the glycerine to be weighed on the analytical balance, and also the nitro-glycerine formed to be brought into a measuring tube accurately divided into twentieths of a c.cm. The apparatus shown in the figure consists of the glycerine pipette A, and the measuring tube B, which is furnished with the cock H, and is enlarged at the top into a very thin-walled nitration vessel N, enclosed in the cooler K. The glycerine pipette is furnished with two marks, which correspond to a weight of glycerine of 10 g., and is closed by means of a glass tap. Both this and the nitration vessel are fixed by means of clamps to the same retort stand. A nitration in this apparatus is carried out in the following manner. The nitration vessel is filled up to above the fixed mark with the nitrating acid and cooled to 15° C., when one allows the excess of acid to run away through the cock H. While the glycerine is allowed to drop from the pipette A into the nitrating acid as slowly as possible, for the purpose of thorough stirring, one conducts through the apparatus a current of air dried by means of concentrated sulphuric acid, and carries away the heat generated in the reaction by a rapid flow of cold water. An observation of the nitration temperature in the small glycerine mass is not necessary, especially if the temperature of the cooling water is only 12-15° C., and it passes through the cooler with an adequate velocity. As soon as the glycerine has run down to the lower mark on the pipette, one shuts the cock of the pipette, allows about another minute's stirring, and then interrupts the air current by shutting the cock H. After standing a quarter of an hour (with the cooling water running) the nitro-glycerine completely separates from the waste acid, whereupon the latter is allowed to run down to the zero mark, when the volume of the former is read off, and from the result is calculated the glycerine contained in the 10 g. weight. Since the read-off and calculated nitro-glycerine gives no proof of the quality of the glycerine used, a nitration must be carried through for comparison under the same experimental conditions on chemically pure 100 per cent glycerine; the result is noted once for all as corresponding to 100 per cent glycerine. For example, 10 g. of a glycerine gave 14·45 c.cm. of nitro-glycerine, and by the nitration for comparison under similar conditions of 100 per cent glycerine, 15 c.cm. of nitro-glycerine were obtained, so is the glycerine under examination, irrespective of the $C_3H_8O_3$ content found by the Hehner or any other method of examination, valued as 14·45 : 15·00 = 96·3 per cent dynamite glycerine.

It is absolutely necessary always to work under the same conditions. It is advantageous to employ for 10 g. glycerine, 60 g. nitrating acid (45 per cent HNO_3 and 55 per cent H_2SO_4) and the reading of the nitro-glycerine volume is made at 15-16° C. Since the size of the yield is chiefly dependent upon the ratio between the glycerine and nitrating acid, the mass of the glycerine used should not much exceed the limits 9·9-10·1 g.

The apparatus permits in an hour an exact estimation to be easily carried out, which represents an advantage over other methods not to be despised, and, since in the purchase of dynamite glycerine differences frequently arise between buyer and seller, owing to defective methods of examination, should be a very welcome laboratory apparatus to the dynamite as well as to the glycerine manufacturer. On account of its simple and solid construction, it is very easily cleaned, and the risk of breakage is only very slight. The manufacture of the apparatus is undertaken by the firm Ephraim Greiner, of Stützerback, Thuringen.

DETERMINATION OF LIME SALTS.

This test, by means of which it is easy to distinguish concentrated from distilled glycerine, is carried out in such a way that the glycerine is diluted with twice or three times its volume of water and ammonium oxalate added ; the presence of lime salts will cause a deposit of calcium oxalate.

The presence of sulphuric acid, generally in the form of calcium sulphate (gypsum), can be ascertained by mixing the diluted glycerine with a solution of barium chloride ; a resultant white deposit proves the presence of sulphuric acid. If the deposit resulting from the barium chloride is soluble in hydrochloric acid, this proves the presence of phosphoric acid also.

TESTS FOR OTHER IMPURITIES.

Glycerine which is somewhat acid can on distillation dissolve iron or copper from the apparatus and hereby become contaminated. These iron compounds can easily be ascertained by the addition of a solution of nitro-prusside sodium or salicylic acid. In both cases red coloration takes place in the presence of iron compounds; the presence of copper can be proved by the addition of ammonia; hereby the glycerine, particularly in thicker layers of the liquid, has a distinctly blue coloration in the presence of copper.

Some kinds of glycerine have a peculiar smell which is either sour or rancid. In the former case it is generally due to formic acid or acetic acid, in the second to butyric acid. Formic acid can be recognized by mixing the glycerine under examination with an ammoniacal silver nitrate solution; in the presence of formic acid, immediate separation of the metallic silver takes place; if the glycerine is pure, on becoming cold, the liquid remains clear, and only on heating reduces the ammoniacal silver oxide to silver metal. Also both acids can be detected by the sense of smell, if the glycerine is mixed with sulphuric acid.

Butyric acid is best detected by the odour; the glycerine is rubbed between the hands and these are brought up to the nose; the presence of butyric acid is at once detected by the unpleasant rancid smell which is peculiar to this acid. Further, this butyric acid test can be carried out in another manner; to this end equal volumes of alcohol and of the glycerine are mixed, and to the mixture sulphuric acid is added; in the presence of butyric acid, butyric ether is formed under these circumstances, and the liquid has a very pleasant and characteristic smell of pine-apple.

Albumen is precipitated by means of tannic acid or in flocks by acidifying with acetic acid.

TEST FOR SUGAR CONTENTS.

Intentional adulteration of glycerine can be made either with grape sugar in the form of starch syrup, or for this purpose the thick syrup of beet sugar factories is used, which in addition to grape sugar also contains cane sugar. We shall give later on the method by which these different sugars can be distinguished from one another. In any case these adulterations with respect to relative prices hardly ever occur now.

As a first test as to probable sugar contents, small quantities of the glycerine to be analysed are mixed with kali lye and concentrated sulphuric acid: if the samples are free from sugar, then they are not altered by these additions: if they contain sugar they will colour brown already when cold or on gentle heating and humic substances arise from the sugar.

It has been proposed to determine the addition of grape sugar by warming glycerine with the so-called Fehling solution (alkaline copper oxide solution) when in the presence of grape sugar red copper protoxide is separated; as, however, pure glycerine gives a deposit in the Fehling solution, this test is hardly applicable. (This does not agree with the translator's experience.)

A very simple method of proving the presence of sugar in glycerine is by means of the polarimeter; glycerine does not cause the plane of polarization to deviate; sugars do, either to the right or to the left. Glycerine which is of too dark a colour to be tested in a polarimeter should be decolorised before the test. This can be accomplished by mixing the glycerine with 0·1 of its volume of lead acetate, shaking and filtering from the residue; on calculating the sugar contents this dilution must be taken into account. It is simpler to filter the glycerine to be tested through dry spodium whereby it is sufficiently decolorized to enable the optical test to be made.

If glycerine containing sugar causes rotation of the plane of polarization, then the question may possibly arise as to whether it has been mixed with potato sugar or also with cane sugar syrup, the latter of which contains different quantities of cane sugar and grape sugar. In order to determine this, it must first be ascertained by how many degrees the plane of polarization has been rotated, and then the sugar must be inverted, that is transformed into invert sugar; this latter takes place by heating the glycerine to be tested for ten minutes with 0·1 of its volume of hydrochloric acid to 70-80° C. If originally the plane moved to the right, and if the rotation, which now owing to the dilution with hydrochloric acid must be reckoned 0·1 higher, remains unaltered, then grape sugar alone was present, if, however, the plane rotates to the left after the original liquid had indicated a movement to the right, then this is a proof that the glycerine contained cane sugar; cane sugar inclines to the right and the resultant invert sugar to the left.

DETERMINATION OF GYLCERINE IN WINE.

In order to determine small quantities of glycerine in wine—an investigation of importance as to the glycerine contents of the wine itself as well as proving whether the wine has been intentionally adulterated the following process according to German official regulations for the testing of wines is adopted:—

(*a*) Determination of glycerines in wines with less than 2 g. sugar in 100 cm.^{3}

One hundred cm.^{3} of wine are evaporated in a porcelain dish over a water-bath to about 10 cm.^{3} and the residue is mixed with about 1 g. quartz sand and so much milk of lime of 10 per cent $Ca(OH)_2$ that to every 1 g. extract 1·5-2 cm.^{3} milk of lime is added, and evaporated practically dry. The damp residue is mixed with about 5 cm.^{3} of alcohol at 96 per cent by weight, the mass attaching to the sides of the porcelain dish are loosened with a spatula and rubbed into a fine paste with a small addition of alcohol at 96 per cent by means of a small pestle. Spatula and pestle are then rinsed with the same strength of alcohol. Constant stirring takes place and the dish is heated in a water-bath until it begins to boil, and the cloudy alcoholic liquid is poured through a small filter into a small receiver of 100 cm.^{3} contents. The powder-like residue remaining in the dish is again stirred with 10-12 cm.^{3} of alcohol, drawn off hot, the extract poured into the 100 cm.^{3} receiver, and this process repeated for so long until the amounts of the extracts are about 65 cm.^{3} the insoluble residue remaining in the dish. Then the small funnel attached to the 100 cm.^{3} receiver is rinsed with alcohol, the alcoholic extract is cooled to 15°, and it is filled with alcohol at 96 per cent to 100 cm.^{3} After vigorous shaking the alcoholic extract is filtered through a plaited filter into a graduated glass cylinder, 90 cm.^{3} filtrate are poured into a glass dish, and evaporated over a hot-water bath avoiding any powerful boiling. The residue is collected with small quantities of absolute alcohol, the solution poured into a divided glass cylinder, provided with a stopper, and the dish is washed with small quantities of absolute alcohol, until the alcohol solution amounts to exactly 15 cm.^{3} To this solution 7·5 cm.^{3} of absolute ether should be added three times, and the solution should be well shaken after each addition. The closed cylinder remains standing until the alcohol ether solution is quite clear; then the solution is poured into a weighing glass fitted with a ground stopper. After the glass cylinder has been rinsed with a mixture (about 5 cm.^{3}) of 1 volume of absolute alcohol, with 1½ volumes of absolute ether, and this liquid has been poured into the weighing glass, the alcoholic ether liquid is evaporated over a hot but not boiling water-bath, when violent boiling of the solution must be avoided. After the residue in the weighing glass has become a thick liquid, the glass is placed in a drying oven between the double partitions of which water is boiling, and after one hour's drying it is left in the exsiccator to cool and weighed.

(*b*) In wines with 2 g. or more sugar in 100 cm.^{3}

Fifty cm.^{3} of wine are heated in a large receiver over a water-bath, mixed with 1 g. quartz sand, and small quantities of milk of lime are added for so long until the mixture which at first turned dark has become clear again and assumed a smell of lye. The mixture is warmed in a water-bath and constantly shaken. When cold, 100 cm.^{3} of alcohol at 96 per cent are added, and the resultant deposit left to settle, the alcoholic solution is filtered off and the deposit washed with alcohol at 96 per cent. The filtrate is evaporated and the residue treated further according to the regulations for wines with lesser sugar contents.

According to the decrees of the Committee of Wine Statistics in Germany it is recommended that an objection on account of addition of glycerine is justified when with a total glycerine content exceeding 0·5 g. in 100 c.cm. wine, the extract residue (extract reduced with respect to non-volatile acids) consists of more than two-thirds glycerine, or, with a proportion of glycerine to alcohol of more than 10 : 100, the total extract does not exceed 1·8 g. per 100 c.cm., or after deduction of the glycerine from the residue extract, 1 g. in 100 c.cm.

DETERMINATION OF GLYCERINE IN BEER.

The determination of the glycerine contained in beer can be carried out as follows:—

50 cm.^{3} of beer are evaporated with about 3 g. calcium hydrate to the thickness of syrup, and then mixed with 10 g. coarse powdered marble or sea sand and left to dry, but the residue should not be quite dry or hard. Then it is completely separated from the dish and boiled with 100-150 cm.^{3} of strong alcohol at about 96 per cent. After filtering, the alcoholic extract is evaporated or distilled, and the residue is again dissolved in 10 cm.^{3} alcohol.

To this solution, 15 cm.^{3} of ether are added in three portions, the solution is thoroughly mixed after each addition and left to settle. The clear ether alcohol solution containing the glycerine is poured off, the residue again treated with 5 cm.^{3} alcohol and shaken with 7·5 cm ^{3} of ether in two portions, when the glycerine remaining in the residue is dissolved. In a weighed weighing glass the ether alcohol solution is evaporated to the thickness of a syrup, and then left to dry an hour in a water-bath drying oven, weighed, and the glycerine tested for the presence of any sugar. Or, the ether alcohol solution containing the glycerine can be evaporated in a platinum dish and, after drying, weighed, when the contents of the dish can be ashed in order to determine any existing mineral substances, and separate them from the glycerine.

CHAPTER XVI.

Investigation of Nitro-Glycerine and Dynamite.

The analysis of nitro-glycerine comprises mostly the qualitative test for acid or alkali: the investigation of dynamite and the determination of its composition is varied according to whether it contains the nitro-glycerine only absorbed or gelatinized. Special methods of investigation should be made for explosive gelatine and gelatine dynamite, and finally certain stability and heat tests come into consideration.

Analysis of Nitro-Glycerine as to Acid and Alkali.

A sample is placed in a separator, distilled water poured over it, and it is well shaken. By the addition of some drops of methyl orange the reaction is ascertained, and after an addition of 1-2 drops of $\frac{N}{4}$ hydrochloric acid the colour should change.

Analysis of Dynamite.

For this purpose Hess's method should be used, which is as follows: The dynamite should be treated with water-free ether, and the remaining oil should be tested by letting a piece of filtering paper absorb it and then detonating on an anvil. If the oil is dissolved in alcohol and mixed with a solution of ammonium sulphide in alcohol, then polysulphide is formed, and later the sulphur separates. If a drop of the oil is placed in a solution of green vitriol mixed with hydrochloric acid, and if this is warmed, then the nitrous oxide reaction should result. If a drop of the nitro-glycerine is added to a potassium iodide starch solution acidified with diluted sulphuric acid and mixed with a few fragments of zinc, then the liquid turns blue. If the oily deposit is evidently uniform, and its specific gravity about 1·6 and it has no particular odour, it may be taken that it is only composed of nitro-glycerine. If impure ether has been used then the impurities will be found in the residue. If there are more than traces of sulphur, paraffin, and resin, they separate from the nitro-glycerine. In order to analyse these, some of the separated substance is taken and pressed between filtering paper. The sulphur separates in the form of crystal and can be recognized thereby as also by its smell and flame on being ignited. If the extract freed from ether is treated with cold alcohol, then paraffin remains behind. Any rosin can, by boiling with a soda solution, be saponified and isolated from the soap by precipitation with hydrochloric acid. Should all three substances be in the dynamite at the same time, the nitro-glycerine should first be decanted and the residue carefully pressed between filtering paper: then by boiling with a soda solution the resin is first separated, and the residue washed with water and dried. Part thereof can be treated with aqua regia in order to transform any existing sulphur into sulphuric acid and this identified in the form of barium-sulphate; another part can be boiled with ammonium sulphide solution when the sulphur dissolves with the formation of ammonium-polysulphide, the paraffin, however, on cooling swims in a crust on the liquid and is then washed with water, dried, and can be further tested. The residue of the extraction is then tested microscopically when kieselguhr, wood meal, and charcoal can be recognized by their construction and colouring. Brown coal and pit coal are distinguished by the nature of their products on dry distillation. Brown coal gives acetic acid or ammonium acetate. If the residue is reduced to ashes, then in addition to wood or coal ashes, other mineral substances are found which can easily be determined by the well-known analytical methods.

QUANTITATIVE EXAMINATION.

Either a weighed amount of dynamite is placed on a dried and weighed linen filter in a funnel and extracted by frequently pouring ether on it, or a weighed amount is mixed with ether in an Erlenmeyer flask shaken frequently, and the whole is filtered on a linen filter and again washed with ether. The ether extract is transferred to a beaker and evaporated on a water-bath at 40°; from the moment the extract clouds, attention should be paid. As soon as the cloudiness disappears again the beaker is placed under the bell of an air-pump, under which there is also calcium chloride in order to remove the last traces of ether and moisture.

If in the dynamite, in addition to nitro-glycerine there is paraffin, resin, sulphur, or similar substances, then the ether-freed extract can be weighed on drying and warmed with a soda solution over a water-bath. Hereby the resin is freed and by decanting and washing with distilled water can be separated from the residue. If to this solution hydrochloric acid is added, the resin precipitates. It can be collected on a filter dried and weighed at 100°, washed, dried, and again weighed.

The nitro-glycerine is extracted from the residue with high percentage alcohol, decanted, and the remaining amounts of paraffin and sulphur are rinsed with strong alcohol, dried and weighed. In order to separate the sulphur from the paraffin, the mass is warmed with an aqueous solution of ammonium sulphide, left to cool, the paraffin layer is broken through, decanted, washed with water, and the paraffin dried and weighed. The quantity of nitro-glycerine and of the sulphur is found from the differences.

The residue remaining from the extraction in so far as it is only composed of fire-proof materials is dried in a stream of dry air at 60° and weighed, then reduced to ashes, and on cooling again weighed, in order to ascertain from any small differences whether small quantities of organic substances were contained in the residue. If it contains other substances as well, then the residue is dried and weighed on the filter, treated with hot distilled water, and the solution evaporated, dried at 120, and the remaining residue again weighed If carbonates are present, the extract, if it contains no chlorates, should be taken up with water again, neutralized with nitric acid, evaporated over the water-bath, dried at 120°, and again weighed. Hereby the carbonates are transformed into nitrates, without modifying the existing extractive substances; from the difference of the two last weights obtained the quantity of carbonic acid can be determined. The dry mass is hereupon heated to redness and on cooling damped with nitric acid, liberated from the free nitric acid again, again heated to redness, and finally on cooling weighed. Then all the water-extracted salts are present as nitrates, and the organic substances destroyed. The difference between the two last weighings accordingly gives the contents in organic soluble substances.

If in the watery extract chlorates were also present, then the carbonic acid must be determined by precipitation with lime determined, and in one part after evaporating and heating to redness the chlorate can be determined in the form of silver chloride. The quantity of nitric acid can be determined in a second part of the extract by changing into ammonia. In the residue from the extraction by water only charcoal or similar organic substances can be contained as well as insoluble absorbents. The organic substances are removed by reducing to ash and the residue is weighed on cooling, whereby the weight of the insoluble mineral substance is ascertained. If several mineral substances are present at the same time, then according to the well-known method they can be determined singly in the residue. If, however, several organic absorbents are present, the proportion can only be approximately determined by means of their elementary composition.

The stability of dynamite is determined by the heat test, and further by a thrice-repeated freezing and melting, as well as by exposure for eight days and nights at 30° with regard to any oozing of the nitro-glycerine. Any inclination to absorb humidity with eventual separation of nitro-glycerine can be tested by exposing over a vessel filled with water for twenty-four hours under a glass bell-jar.

Testing of Explosive Gelatine and Gelatine Dynamite.

The analysis according to Hess is as follows:—

Qualitative Analysis. A slice is cut out of the middle of the cartridge with a knife of wood or horn and cut up into small pieces placed in a small receiver, and a mixture of 2 parts of water-free ether and 1 part water-free alcohol is poured over it. Thereby the nitro-glycerine, collodion cotton, as well as other admixtures of camphor, resin, paraffin, and sulphur are dissolved. The extract is mixed with an excess of chloroform, which precipitates the collodion cotton. The solution above it is poured off, and the residue is pressed between filtering paper. The separated collodion cotton is recognized by its combustibility and its explosiveness caused by shock, as well as its behaviour in the presence of sodium sulphide solution from which it is freed by boiling. On boiling with hydrochloric acid and sulphate of iron a nitrous oxide reaction is given.

The poured-off solution is heated to 30° whereby the largest part of the ether, alcohol, and chloroform evaporates. Then the temperature is raised to 80° whereby these solvents are completely removed. The residue is treated in the same manner as was described for dynamite. Should there be still trinitro-cellulose in the residue freed from chlorates and nitrates, they can be ascertained as follows:—

1. By observation under a microscope with polarized light. The trinitro-cellulose shows a blue colour, the non-nitrated cellulose a red-yellow play of colour.

2. By boiling the residue with hydrochloric acid and sulphate of iron, whereby the nitro-cellulose gives a nitrous oxide reaction.

3. By boiling the residue with alcoholic caustic potash solution and filtering. If the filtrate is slightly acidified by sulphuric acid, it indicates free nitric acid or nitrous acid.

QUANTITATIVE INVESTIGATION.

An average sample is taken and divided with a horn spatula into small pieces, and it is left for five to six days in an exsiccator over calcium chloride to determine the moisture contents.

The best means of removing the nitro-glycerine and the collodion cotton from the gelatine explosive is to treat with alcohol. This is best accomplished in an Erlenmeyer flask in which 5 g. of the finely divided gelatinous explosive is placed, 200 cm.^{3} ether alcohol poured over it, constantly shaken, and left for some hours; the solution is mixed with an excess of chloroform and the remaining mixture is filtered through a dry and weighed filter. By heating on a water-bath to 30° the filtrate is freed from the ether alcohol. If camphor is contained therein, then the residue is shaken with carbon bisulphide. The ether extract can' at once be filtered and the nitro-cellulose precipitated by chloroform from the filtrate, but this is a less accurate method.

The residue remaining on the filter can still contain nitro-cellulose as well as zumic powder. It is dried at 60° in a dry stream of air and then weighed. Then the process is continued as in the case of dynamite. Part of the residue can be boiled with a concentrated solution of sodium sulphide whereby the trinitro-cellulose is dissolved. The solution is filtered through a weighed filter, washed carefully with water, dried, and weighed. From the loss in weight the trinitro-cellulose content can be determined. Another part of the residue is treated with hydrochloric acid, whereby the carbonate and other bases go into solution and can be determined, whereas the dried and washed residue then only contains organic and mineral (insoluble in hydrochloric acid) absorbents. By reducing to ash, the organic substances can be determined from the difference.

STABILITY AND HEAT TESTS.

The stability and heat tests are carried out mostly according to the English methods. Since the commencement of decomposition makes itself apparent through the splitting off of nitrous acid, these tests are based on the detection of this, which is effected with the aid of potassium-iodide paper, or better, starch-iodide paper. Nitrous acid liberates iodine from potassium iodide, which with starch paste gives a deep blue compound of starch iodide. The test, which requires special apparatus, is usually carried out at 160° F. (71° C.).

THE END.

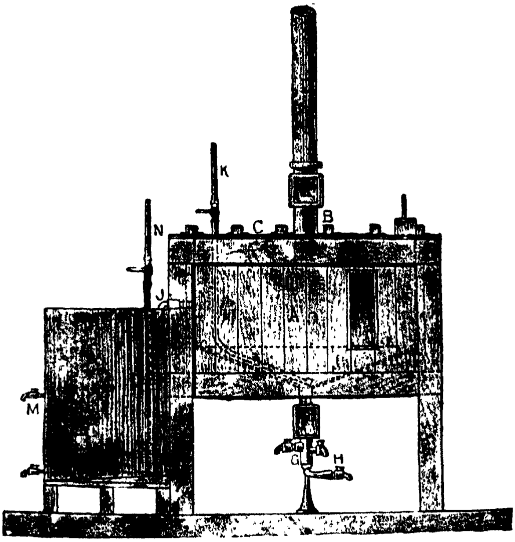

FIG. 5.—(See page 86.)

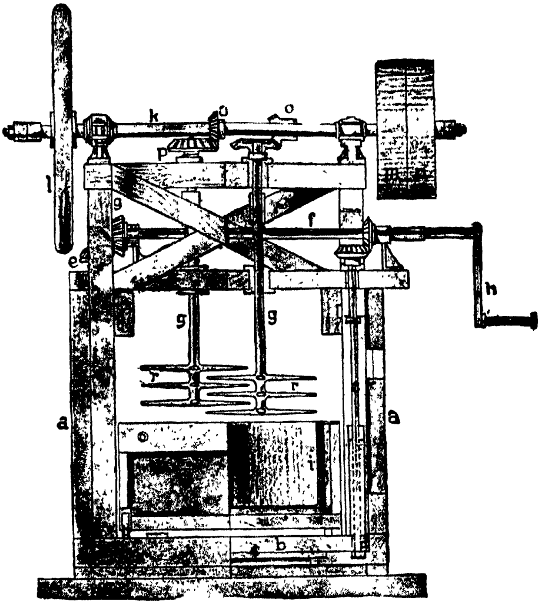

Fig. 6.—(See page 123.)

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